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MORPHOLOGICAL AND STRUCTURAL CRYSTALLOG- RAPHY AND OPTICAL PROPERTIES OF SILICON CARBIDE (SiC)*

PART II: STRUCTURAL CRYSTALLOGRAPHY AND OPTICAL PROPERTIES

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ABSTRACT

X-ray studies were made of β -SiC and five types of α -SiC by means of powder, rotation and equi-inclination Weissenberg photographs. The following data were obtained: α -SiC, a_0 of all types when referred to smallest hexagonal cell = 3.073 Å; c_0 of all types integrally related, type I = 37.70 Å, type II = 15.07 Å, type III = 10.053 Å, type IV = 52.78 Å,

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type VI = 82.94 Å. Formula weights in smallest hexagonal cell = 15, 6, 4, 21, 33, respectively. Calculated density of all α -SiC types = 3.217; observed density, type II = 3.218. Space group, types I, IV, VI = C_{3v}^5-R3m ; types II and III = C_{6v}^4-C6mc . Beta SiC: $a_0 = 4.349$, formula weights in unit cell = 4, calculated density = 3.216, space group = T_d^2-F43m .

All α -SiC types are uniaxial positive. The dichroism varies considerably depending on the color, and both absorptions $\omega > \epsilon$ and $\epsilon > \omega$ were observed. The indices of refraction of all types are essentially the same, but some variation occurs within a given type: $\omega_{Na} = 2.6467-2.6487$, $\epsilon_{Na} = 2.6889-2.6930$. Dispersion (4360-6200 Å): $\omega = .0918$, $\epsilon = .1028$. Beta SiC was found to be transparent yellow to olive green, isotropic, n for red (essentially Li) light about 2.63.

The value of the study is not limited to SiC, for it may be considered the prototype of polytypic substances, many of which exist, but have not yet been studied in detail.

STRUCTURAL CRYSTALLOGRAPHY

REVIEW OF LITERATURE

Rinne (1915), (1916) published a Laue photograph of an unspecified type of SiC which was x -rayed perpendicular to the base. The presence of six-fold symmetry was said to be due to twinning, (0001) being the twinning plane.

Burdick and Owen (1918) investigated SiC of unknown type. They deduced an atomic arrangement whereby both the silicon and carbon atoms occupied face-centered rhombohedral lattices which were almost cubic, one displaced with respect to the other 0.36 of the (0001) spacing.

Hull (1919) stated that the structural arrangement of SiC was similar to that of the diamond except that half the carbon atoms, those of one of the face-centered lattices, were replaced by silicon.

Later Hull (1920) found that the powder photograph of an unknown type of SiC showed lines indicating a close-packed hexagonal structure as well as a diamond-type lattice. He concluded that there were, within the same crystal, both cubic and hexagonal close-packing of silicon atoms with carbon atoms at the centers of the tetrahedrons.

Hauer and Koller (1920) published Laue photographs perpendicular to the base of hexagonal (α) SiC, types I, II and III. Although each diagram was unique, there were many spots common to two, and a few common to all three of the SiC types. They also made a similar Laue photograph of a coalescence of types I and II. The diagram consisted of the type I pattern upon which was superposed the strongest spots of type II, equivalent spots being coincident.

Espig (1921) made Laue photographs perpendicular to (0001) and (10 $\bar{1}$ 0) of all three of the α -SiC types. Several very thin basal sections cut from different type II crystals were x -rayed perpendicular to (0001), but all showed hexagonal symmetry, disproving the assumption of Rinne that the hexagonal pattern was due to twinning. Rotation photographs were

made of type II α -SiC using Mo radiation. The smallest cell fulfilling the wave-length requirements of the Laue photographs was said to be hexagonal with: $a_0 = 6.2 \text{ \AA}$; $c_0 = 15.3 \text{ \AA}$. It contained 24 formula weights, and the most probable space group was given as C_{6v}^4 . Espig postulated the same unit cell for types I and III α -SiC but different arrangements within the cell, but no details were given.

Ott (1925a) gave complete structure data for type II α -SiC. The hexagonal unit cell dimensions obtained from rotation photographs using Mo radiation were: $a_0 = 3.09_5 \text{ \AA}$; $c_0 = 15.17 \text{ \AA}$. The $c_0:a_0$ ratio was thus 4.90 and the number of formula weights per cell was 6. Atomic co-ordinates were given as:

C: 0, 0, 0; 0, 0, $3/6$; $1/3$, $2/3$, $1/6$; $1/3$, $2/3$, $5/6$; $2/3$, $1/3$, $2/6$; $2/3$, $1/3$, $4/6$
 Si: 0, 0, p ; 0, 0, $3/6+p$; $1/3$, $2/3$, $1/6+p$; $1/3$, $2/3$, $5/6+p$; $2/3$, $1/3$, $2/6+p$; $2/3$, $1/3$, $4/6+p$; where $p = 1/8$.

The structure was said to consist of an atom of one kind, for example C, surrounded exactly tetrahedrally by four atoms of the other kind, Si, the smallest C-Si distance being 1.9_0 \AA . The space group was given as C_6^6 .

Ott's second publication (1925b) discussed the structure of type I α -SiC. The dimensions of the smallest hexagonal cell as determined from rotation photographs were: $a_0 = 3.09_5 \text{ \AA}$, $c_0 = 37.9_5 \text{ \AA}$. The type actually was based on a rhombohedral cell containing five formula weights: $a_{rh} = 12.7_8 \text{ \AA}$ and $\alpha = 13^\circ 55'$. A possible space group was given as C_3^4 . Atomic co-ordinates in the hexagonal cell were:

C: 5 atoms at 0, 0, 0; 0, 0, $2/15$; 0, 0, $6/15$; 0, 0, $9/15$; 0, 0, $13/15$
 5 atoms in similar arrangement from $-1/3$, $1/3$, $1/3$
 5 atoms in similar arrangement from $1/3$, $-1/3$, $2/3$
 Si: 15 atoms at the C positions $+0$, 0, p , where $p = 1/20$.

In a third paper, Ott (1926) reported on the structure of α -SiC, type III, and upon the so-called "amorphous" carbide. The unit cell of α -SiC, type III, was found to be hexagonal with $a_0 = 3.09_5 \text{ \AA}$ and $c_0 = 10.0_9 \text{ \AA}$ and to contain four formula weights. Within the limits of error of the measurements, both the c_0 value and the axial ratio were rationally related to similar values obtained for types I and II. Atomic co-ordinates of the structure were:

C: 0, 0, 0; 0, 0, $1/2$; $1/3$, $-1/3$, $1/4$; $-1/3$, $1/3$, $3/4$
 Si: 0, 0, p ; 0, 0, $1/2+p$; $1/3$, $-1/3$, $1/4+p$; $-1/3$, $1/3$, $3/4+p$, where $p = 3/16$.

Gray aggregates of the "amorphous" carbide were studied by the x-ray powder diffraction method using copper radiation. They were found to be a mixture of a cubic ZnS-type substance with $a_0 = 4.37 \text{ \AA}$ —assumed to be cubic SiC—and a minor amount of α -SiC, type II.

Ott pointed out that the same exactly tetrahedral arrangement of C and Si atoms was the fundamental unit of all the SiC structures, and that the unit cells of the α -SiC types differed only in the manner in which these tetrahedrons were built up in the direction of the c -axis. The coalescence of types was readily explained since all the hexagonal modifications were similar in the plane of the a axes, the contact plane of the coalescences.

Becker (1927) gave $a_0 = 4.30 \text{ \AA}$ as the cell dimension of yellow cubic SiC.

Ott (1928) described α -SiC, type V. Rotation photographs indicated the unusual hexagonal cell: $a_0 = 3.09_5 \text{ \AA}$, $c_0 = 129.0_3 \text{ \AA}$; the type was actually based on a rhombohedral lattice with $a_{rh} = 41.1_5 \text{ \AA}$, $\alpha = 4^\circ 06'$, and contained 17 formula weights. No attempt was made to determine the atomic positions, but the relationship to the other types made it seem probable that the same tetrahedral arrangement of C and Si atoms existed here also.

Braekken (1930) examined a minute black "octahedral" crystal found in commercial SiC, and assumed to be cubic SiC. It had a ZnS-type structure with $a_0 = 4.348 \pm .005 \text{ \AA}$.

The data given by Ewald and Hermann in the *Strukturbericht I* (1931) and by Wyckoff (1931) agree with those given by Ott, except that they place α -SiC, type I, in space group C_{3v}^5 , and types II and III in group C_{6v}^4 .

Hengstenber and Garrido (1932) made a Fourier analysis showing the electron density normal to the basal pinacoid of an unspecified type of hexagonal SiC. The results were in harmony with the calculations of Ott that in the c direction carbon planes are about 2.53 \AA apart and that silicon planes lie about 1.90 \AA above the carbon.

Borrmann and Seyfarth (1933) gave the following data for type II SiC: $a_0 = 3.076 \pm 0.003 \text{ \AA}$; $c_0 = 15.07 \pm 0.015 \text{ \AA}$. The calculated density was 3.212 which the authors confirmed by the suspension method, although the value for the density determined in this manner was not given.

Hanawalt, Rinn and Frevel (1938) published powder photograph data for cubic and commercial SiC. The latter was said to be a mixture of cubic and hexagonal forms.

Tone (1938) stated that, in spite of the different known types of this substance, all lots of hexagonal crystals gave the same x-ray powder diffraction pattern irrespective of the source of the sample, and that lines of cubic as well as of hexagonal SiC were present in the pattern. He published a series of Laue photographs of α -SiC taken perpendicular to the base, and stated that the diagrams seemed to show a gradual transition from one type to another. No explanation was offered except that some of the differences were thought to be due to twinning.

Benner, Melton and Boyer (1940) gave 4.36_3 \AA as the lattice constant of a "typical" sample of cubic SiC, and stated that the constant varied with amount of impurity to a minimum of 4.35 \AA . No chemical data were given.

Baumann (1941) gave *x*-ray powder diffraction data for SiC (type or types not stated).

LAUE PHOTOGRAPHS

If the new method of notation used in connection with the observed crystal faces for the various α -SiC types (see Table 16) is applied to the Laue photographs of Hauer and Koller (1920), the relationship between the spots of the Laue photographs of the various types is immediately evident; again only those spots are common to two or more types whose indices are equivalent when referred to the greatest common divisor $c:a$ value.

From the Laue photographs published by Hauer and Koller, Espig, and Ott, and from the observations of coalescences of α -SiC types made by Baumhauer and the writer, it seems quite certain that the Laue patterns illustrated by Tone (1938) are "transitional" because they are from crystals consisting of coalescences of types I and II in different proportions. One of his patterns is apparently influenced by a type I twin in which the *c* axis is the twinning axis.

The numerous satisfactory Laue photographs reproduced in the literature clearly indicate that the centro-symmetrical crystal class of α -SiC, type I, is D_{3d} , and that of types II and III is D_{6h} . Because of this and the very close morphological relationship of the new types IV and VI to the well-known type I, no Laue exposures were made during the present study.

POWDER PHOTOGRAPHS

Introduction. Because of the common occurrence of coalescences and twinning of the various α -SiC modifications, extreme care was taken in the selection of crystals of each type to be prepared for the powder photographs. Well-developed, unstriated crystals of types I, II and III were employed, while small pieces were chipped from the edges of the large basal pinacoids of types IV and VI. It was not possible to select entirely isotropic individuals of β -SiC. Instead, masses containing a minimum amount of anisotropic material were crushed for the photographs. As additional checks, at least two powder photographs were made of each of the modifications, different samples being used in each case. The fact that in all cases the different powder photographs of the same type of α -SiC were identical indicates that a desired hexagonal modification can unequivocally be selected by careful goniometric study.

All the exposures were made with filtered Cu x -radiation using a camera of about 57.3 mm. diameter, a later modification of the type described by Buerger (1936). The camera was standardized with NaCl.

Pattern of Each SiC Modification. Data from the powder photographs of each SiC modification are given in Tables 18–23 inclusive. Values are for the $\text{CuK}\alpha_1$ lines where resolved, otherwise for $\text{CuK}\alpha_1$ and α_2 . The intensity values were derived from visual comparisons of the line intensities using an arbitrary scale in which the weakest line in each photograph was numbered 1 and the strongest, 10. In the case of α -SiC the planes giving rise to the lines on the powder photographs were ascertained by correlation with those giving Weissenberg spots on the zero and first levels of a -axis rotations. The films of β -SiC were indexed by the use of the chart published by Lukesh and Chesley (1941), as well as by correlation with Weissenberg data. The calculated values of $d_{hk.l}$ for the hexagonal modifications were derived from $a_0 = 3.073 \text{ \AA}$ and the $c:a$ ratios obtained from goniometric study; those for β -SiC were based on $a_0 = 4.349 \text{ \AA}$.

Figure 12 compares the powder photographs of the various SiC modifications. A few lines, indicated by asterisks, are due to quartz from the agate mortar used for final grinding of the specimens.

Cell Dimensions and Density. Because of the discrepancies in the literature concerning the cell dimensions and the calculated and observed densities of the hexagonal SiC types, it was thought worth while to make as precise determinations of these properties as equipment and samples available would permit, and to use analyzed material.

TABLE 18. DATA FROM X-RAY POWDER PHOTOGRAPHS OF α -SiC, TYPE I

Line No.	Intensity	$hk.l$	$d_{hk.l} \text{ (\AA)}$	
			Observed	Calculated
1	4	$\left\{ \begin{smallmatrix} 10.1 \\ 01.2 \end{smallmatrix} \right\}$	2.66	$\left\{ \begin{smallmatrix} 2.65 \\ 2.64 \end{smallmatrix} \right\}$
2	7	10.4	2.58	2.56
3	7	$\left\{ \begin{smallmatrix} 00.15 \\ 01.5 \end{smallmatrix} \right\}$	2.51	$\left\{ \begin{smallmatrix} 2.51 \\ 2.51 \end{smallmatrix} \right\}$
4	6	10.7	2.40	2.39
5	5	01.8	2.32	2.32
6	1	10.10	2.19	2.17
7	3	01.11	2.11	2.10
8	1	10.13	1.97	1.96
9	2	01.17	1.70	1.70
10	5	10.19	1.59	1.59
11	9	$\left\{ \begin{smallmatrix} 01.20 \\ 11.0 \end{smallmatrix} \right\}$	1.54	$\left\{ \begin{smallmatrix} 1.54 \\ 1.54 \end{smallmatrix} \right\}$

TABLE 18 (Type I, *continued*)

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
12	5	10.22	1.444	1.441
13	4	01.23	1.398	1.396
14	2	02.4	1.320	1.318
15	8	{10.25}	1.311	{1.312}
		{11.15}		{1.311}
		{20.5}		{1.310}
16	2	02.7	1.297	1.292
17	2	20.8	1.281	1.281
18	2	{00.30}	1.257	{1.257}
		{02.10?}		{1.255}
19	1	20.11	1.246	1.241
20	1	20.17	1.143	1.141
21	3	02.19	1.106	1.105
22	2	20.20	1.089	1.087
23	4	02.22	1.053	1.051
24	4	20.23	1.035	1.033
25	1	10.34	1.024	1.023
26	5	{01.35}	1.000	{.998}
		{02.25?}		{.998}
		{21.4}		{1.000}
		{12.5}		{.997}
27	3	21.7	.990	.989
28	3	12.8	.984	.984
29	5	{11.30}	.974	{.973}
		{21.10?}		{.972}
30	1	12.11	.965	.965
31	4	10.37	.952	.952
32	4	01.38	.930	.930
33	1	12.17	.917	.916
34	4	21.19	.896	.897
35	7	{10.40}	.888	{.888}
		{12.20}		{.887}
		{30.0}		{.887}
36	6	{01.41}	.868	{.869}
		{21.22}		{.868}
37	5	12.23	.858	.857
38	1	02.34	.851	.852
39	10	{00.45}	.838	{.838}
		{20.35}		{.837}
		{21.25}		{.837}
		{20.15}		{.837}
40	4	12.26	.827	.826
41	5	02.37	.809	.809
42	6	20.38	.796	.795

TABLE 19. DATA FROM X-RAY POWDER PHOTOGRAPHS OF α -SiC, TYPE II

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
1	6	10.1	2.61	2.62
2	7	{00.6}	2.51	{2.51}
		{10.2}		{2.51}
3	5	10.3	2.36	2.35
4	4	10.4	2.19	2.17
5	3	10.5	2.00	2.00
6	3	10.7	1.67	1.67
7	8	{10.8}	1.54	{1.54}
		{11.0}		{1.54}
8	5	10.9	1.419	1.418
9	3	20.1	1.329	1.326
		{10.10}		{1.312}
10	8	{11.6}	1.309	{1.311}
		{20.2}		{1.310}
11	3	20.3	1.285	1.286
12	3	{00.12}	1.253	{1.257}
		{20.4}		{1.255}
13	2	{10.11}	1.217	{1.219}
		{20.5}		{1.217}
14	2	20.7	1.131	1.132
15	4	20.8	1.087	1.087
16	1	10.13	1.061	1.063
17	4	20.9	1.042	1.042
18	3	12.1	1.002	1.004
		{10.14}		{.998}
19	5	{20.10}	.997	{.998}
		{12.2}		{.997}
20	4	12.3	.986	.986
21	5	{11.12}	.972	{.973}
		{12.4}		{.972}
22	2	{20.11}	.953	{.955}
		{12.5}		{.954}
23	4	10.15	.940	.940
24	3	12.7	.911	.911
		{10.16}		{.888}
25	9	{12.8}	.888	{.887}
		{30.0}		{.887}
26	1	20.13	.873	.874
27	6	12.9	.862	.862
28	2	10.17	.841	.842
		{00.18}		{.838}
29	10	{20.14}	.837	{.837}
		{12.10}		{.837}
		{30.6}		{.837}
30	3	12.11	.811	.811
31	5	20.15	.802	.802

TABLE 20. DATA FROM X-RAY POWDER PHOTOGRAPHS OF α -SiC, TYPE III

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
1	4	10.0	2.67	2.66
2	5	10.1	2.59	2.57
3	4	00.4	2.52	2.51
4	5	10.2	2.36	2.35
5	3	10.3	2.08	2.08
6	2	10.4	1.83	1.83
7	4	10.5	1.61	1.60
8	6	11.0	1.54	1.54
9	5	10.6	1.419	1.418
10	7	11.4	1.311	1.311
11	4	20.2	1.287	1.286
12	3	10.7	1.264	1.264
13	2	20.3	1.238	1.237
14	2	20.4	1.178	1.176
15	1	10.8	1.136	1.136
16	4	20.5	1.111	1.110
17	5	20.6	1.042	1.042
18	3	10.9	1.030	1.030
19	4	12.1	1.000	1.001
20	5	12.2	.985	.986
21	4	$\left\{ \begin{smallmatrix} 20.7? \\ 11.8 \end{smallmatrix} \right\}$.973	$\left\{ \begin{smallmatrix} .976 \\ .973 \end{smallmatrix} \right\}$
22	3	12.3	.963	.963
23	5	10.10	.941	.940
24	2	12.4	.933	.934
25	1	20.8	.912	.914
26	4	12.5	.899	.900
27	6	30.0	.887	.887
28	10	$\left\{ \begin{smallmatrix} 10.11 \\ 12.6 \end{smallmatrix} \right\}$.863	$\left\{ \begin{smallmatrix} .864 \\ .862 \end{smallmatrix} \right\}$
29	3	20.9	.856	.856
30	8	$\left\{ \begin{smallmatrix} 00.12 \\ 30.4 \end{smallmatrix} \right\}$.837	$\left\{ \begin{smallmatrix} .838 \\ .837 \end{smallmatrix} \right\}$
31	4	12.7	.824	.824
32	9	20.10	.803	.802
33	1	10.12	.798	.799
34	3	12.8	.786	.785

TABLE 21. DATA FROM X-RAY POWDER PHOTOGRAPHS OF α -SiC, TYPE IV

Line No.	Intensity	$hk.l$	$d_{hk.l}$ (Å)	
			Observed	Calculated
1 broad	7	$\left\{ \begin{array}{l} 01.2? \\ 10.4 \\ 01.5 \end{array} \right\}$	2.63	$\left\{ \begin{array}{l} 2.65 \\ 2.61 \\ 2.58 \end{array} \right\}$
2	10	$\left\{ \begin{array}{l} 00.21 \\ 10.7 \end{array} \right\}$	2.53	$\left\{ \begin{array}{l} 2.51 \\ 2.51 \end{array} \right\}$
3	2	01.8	2.47	2.47
4	2	10.10	2.40	2.38
5	1	01.11	2.35	2.33
6	1	10.13	2.23	2.23
7	1	01.14	2.17	2.17
8 broad	3	$\left\{ \begin{array}{l} 10.16? \\ 01.17 \end{array} \right\}$	2.01	$\left\{ \begin{array}{l} 2.07 \\ 2.02 \end{array} \right\}$
9	1	10.25	1.66	1.65
10	1	01.26	1.62	1.61
11	8	$\left\{ \begin{array}{l} 10.28 \\ 11.0 \end{array} \right\}$	1.54	$\left\{ \begin{array}{l} 1.54 \\ 1.54 \end{array} \right\}$
12	2	01.29	1.51	1.50
13	3	10.31	1.442	1.434
14	2	01.32	1.407	1.402
15	1	10.34	1.337	1.341
		$\left\{ \begin{array}{l} 01.35 \\ 11.21 \end{array} \right\}$		$\left\{ \begin{array}{l} 1.312 \\ 1.311 \end{array} \right\}$
16	7	$\left\{ \begin{array}{l} 20.5? \\ 02.7 \\ 20.8? \end{array} \right\}$	1.311	$\left\{ \begin{array}{l} 1.310 \\ 1.310 \\ 1.304 \end{array} \right\}$
17	1	02.10	1.293	1.290
		$\left\{ \begin{array}{l} 00.42 \\ 10.37 \end{array} \right\}$		$\left\{ \begin{array}{l} 1.257 \\ 1.257 \end{array} \right\}$
18	3	$\left\{ \begin{array}{l} 20.14? \\ 01.38 \end{array} \right\}$	1.259	$\left\{ \begin{array}{l} 1.255 \\ 1.231 \end{array} \right\}$
19	1	01.38	1.229	1.231
20	1	20.26	1.114	1.113
21	2	02.28	1.089	1.087
22	2	20.29	1.076	1.074
23	2	$\left\{ \begin{array}{l} 10.46? \\ 02.31 \end{array} \right\}$	1.050	$\left\{ \begin{array}{l} 1.054 \\ 1.048 \end{array} \right\}$
24	2	$\left\{ \begin{array}{l} 01.47? \\ 20.32 \end{array} \right\}$	1.035	$\left\{ \begin{array}{l} 1.035 \\ 1.036 \end{array} \right\}$
		$\left\{ \begin{array}{l} 10.49 \\ 20.35 \end{array} \right\}$		$\left\{ \begin{array}{l} .998 \\ .998 \end{array} \right\}$
25	5	$\left\{ \begin{array}{l} 21.4? \\ 12.5 \\ 21.7 \\ 12.8? \end{array} \right\}$.999	$\left\{ \begin{array}{l} 1.003 \\ 1.001 \\ .997 \\ .994 \end{array} \right\}$

TABLE 21 (Type IV, *continued*)

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
26	2	$\left\{ \begin{array}{l} 21.10 \\ 12.11? \\ 11.42 \end{array} \right\}$.986	$\left\{ \begin{array}{l} .988 \\ .984 \\ .973 \end{array} \right\}$
27	4	$\left\{ \begin{array}{l} 21.13? \\ 12.14? \\ 20.38? \end{array} \right\}$.973	$\left\{ \begin{array}{l} .976 \\ .972 \\ .961 \end{array} \right\}$
28	1	$\left\{ \begin{array}{l} 21.16? \end{array} \right\}$.962	$\left\{ \begin{array}{l} .962 \end{array} \right\}$
29	2	10.52	.948	.948
30	2	01.53	.932	.933
31	1	21.25	.906	.908
32	3	$\left\{ \begin{array}{l} 10.55 \\ 12.26 \end{array} \right\}$.902	$\left\{ \begin{array}{l} .903 \\ .901 \end{array} \right\}$
		01.56		.888
33	7	$\left\{ \begin{array}{l} 21.28 \\ 30.0 \end{array} \right\}$.888	$\left\{ \begin{array}{l} .887 \\ .887 \end{array} \right\}$
34	2	12.29	.881	.880
35	3	21.31	.867	.866
		$\left\{ \begin{array}{l} 10.58? \end{array} \right\}$		$\left\{ \begin{array}{l} .861 \end{array} \right\}$
36	4	$\left\{ \begin{array}{l} 20.47 \\ 12.32 \end{array} \right\}$.858	$\left\{ \begin{array}{l} .858 \\ .859 \end{array} \right\}$
37	2	21.34	.844	.844
		$\left\{ \begin{array}{l} 00.63 \end{array} \right\}$		$\left\{ \begin{array}{l} .838 \end{array} \right\}$
38	9	$\left\{ \begin{array}{l} 02.49 \\ 12.35 \\ 30.21 \end{array} \right\}$.837	$\left\{ \begin{array}{l} .837 \\ .837 \\ .837 \end{array} \right\}$
39	2	20.50	.828	.827
40	2	21.37	.824	.822
41	1	12.38	.815	.815
42	3	02.52	.807	.807
43	3	20.53	.797	.797
44	5	02.55	.779	.778

TABLE 22. DATA FROM X-RAY POWDER PHOTOGRAPHS OF α -SiC, TYPE VI

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
1 very broad	5	$\left\{ \begin{array}{l} 10.4? \\ 01.5 \\ 10.7 \\ 00.33 \end{array} \right\}$	2.63	$\left\{ \begin{array}{l} 2.64 \\ 2.63 \\ 2.60 \\ 2.51 \end{array} \right\}$
2 broad	10	$\left\{ \begin{array}{l} 10.10 \\ 01.11 \\ 10.16 \end{array} \right\}$	2.53	$\left\{ \begin{array}{l} 2.53 \\ 2.51 \\ 2.37 \end{array} \right\}$
3 broad	6	$\left\{ \begin{array}{l} 01.17 \\ 10.22 \\ 01.23 \end{array} \right\}$	2.38	$\left\{ \begin{array}{l} 2.34 \\ 2.17 \\ 2.14 \end{array} \right\}$
4 broad	3	$\left\{ \begin{array}{l} 01.26 \\ 10.28 \end{array} \right\}$	2.18	$\left\{ \begin{array}{l} 2.05 \\ 2.04 \end{array} \right\}$
5	2	10.38	2.05	1.98
6	2	01.38	2.00	1.69
7	2	10.40	1.69	1.69
8	2	10.43	1.64	1.64
9	3	$\left\{ \begin{array}{l} 01.44 \\ 11.0 \end{array} \right\}$	1.56	$\left\{ \begin{array}{l} 1.54 \\ 1.54 \end{array} \right\}$
10	8	10.46	1.54	1.493
11	1	10.49	1.497	1.428
12	3	01.50	1.434	1.408
13	3	$\left\{ \begin{array}{l} 10.55? \\ 11.33 \\ 02.10 \\ 20.11 \end{array} \right\}$	1.410	$\left\{ \begin{array}{l} 1.312 \\ 1.311 \\ 1.314 \\ 1.310 \end{array} \right\}$
14	7	$\left\{ \begin{array}{l} 01.56 \\ 02.16 \end{array} \right\}$	1.313	$\left\{ \begin{array}{l} 1.294 \\ 1.289 \end{array} \right\}$
15	3	$\left\{ \begin{array}{l} 00.66 \\ 02.22? \end{array} \right\}$	1.291	$\left\{ \begin{array}{l} 1.257 \\ 1.255 \end{array} \right\}$
16	3	$\left\{ \begin{array}{l} 02.43 \\ 20.44 \end{array} \right\}$	1.260	$\left\{ \begin{array}{l} 1.095 \\ 1.087 \end{array} \right\}$
17 broad	2	$\left\{ \begin{array}{l} 01.71? \\ 02.46 \end{array} \right\}$	1.091	$\left\{ \begin{array}{l} 1.070 \\ 1.071 \end{array} \right\}$
18	1	$\left\{ \begin{array}{l} 02.49 \\ 20.50 \end{array} \right\}$	1.072	$\left\{ \begin{array}{l} 1.046 \\ 1.038 \end{array} \right\}$
19 broad	3	$\left\{ \begin{array}{l} 01.77 \\ 02.55 \end{array} \right\}$	1.044	$\left\{ \begin{array}{l} .998 \\ .998 \end{array} \right\}$
20	4	$\left\{ \begin{array}{l} 12.5? \\ 21.7? \\ 21.10 \\ 12.11 \end{array} \right\}$.999	$\left\{ \begin{array}{l} 1.004 \\ 1.002 \\ .999 \\ .997 \end{array} \right\}$
21	4	$\left\{ \begin{array}{l} 21.16 \\ 12.17 \end{array} \right\}$.988	$\left\{ \begin{array}{l} .987 \\ .985 \end{array} \right\}$
22	4	$\left\{ \begin{array}{l} 11.66 \\ 21.22? \end{array} \right\}$.975	$\left\{ \begin{array}{l} .973 \\ .972 \end{array} \right\}$

TABLE 22 (Type VI, *continued*)

Line No.	Intensity	$h\bar{k}.l$	$d_{h\bar{k}.l}$ (Å)	
			Observed	Calculated
23	3	10.82	.947	.945
24	3	01.83	.936	.935
25	2	12.38	.914	.914
26	2	$\left\{ \begin{array}{l} 01.86? \\ 21.40? \end{array} \right\}$.905	$\left\{ \begin{array}{l} .907 \\ .905 \end{array} \right\}$
27	2	21.43	.891	.892
28	5	$\left\{ \begin{array}{l} 10.88 \\ 12.44 \\ 30.0 \end{array} \right\}$.888	$\left\{ \begin{array}{l} .888 \\ .887 \\ .887 \end{array} \right\}$
29	2	01.89	.880	.880
30	4	21.49	.867	.865
31	4	12.50	.860	.860
32	1	02.76	.844	.844
33	7	$\left\{ \begin{array}{l} 00.99 \\ 10.94? \\ 20.77 \\ 21.55? \end{array} \right\}$.838	$\left\{ \begin{array}{l} .838 \\ .837 \\ .837 \\ .837 \end{array} \right\}$
		30.33		
34	2	02.82	.806	.805
35	3	20.83	.799	.799
36	1	20.86	.781	.781

TABLE 23. DATA FROM X-RAY POWDER PHOTOGRAPHS OF BETA SiC

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
1	10	111	2.51	2.51
2	1	200	2.18	2.18
3	6	220	1.54	1.54
4	6	311	1.310	1.311
5	1	222	1.256	1.255
6	2	400	1.087	1.087
7	5	331	.998	.998
8	3	420	.972	.972
9	8	422	.888	.888
10	10	$\left\{ \begin{array}{l} 333 \\ 511 \end{array} \right\}$.837	.837

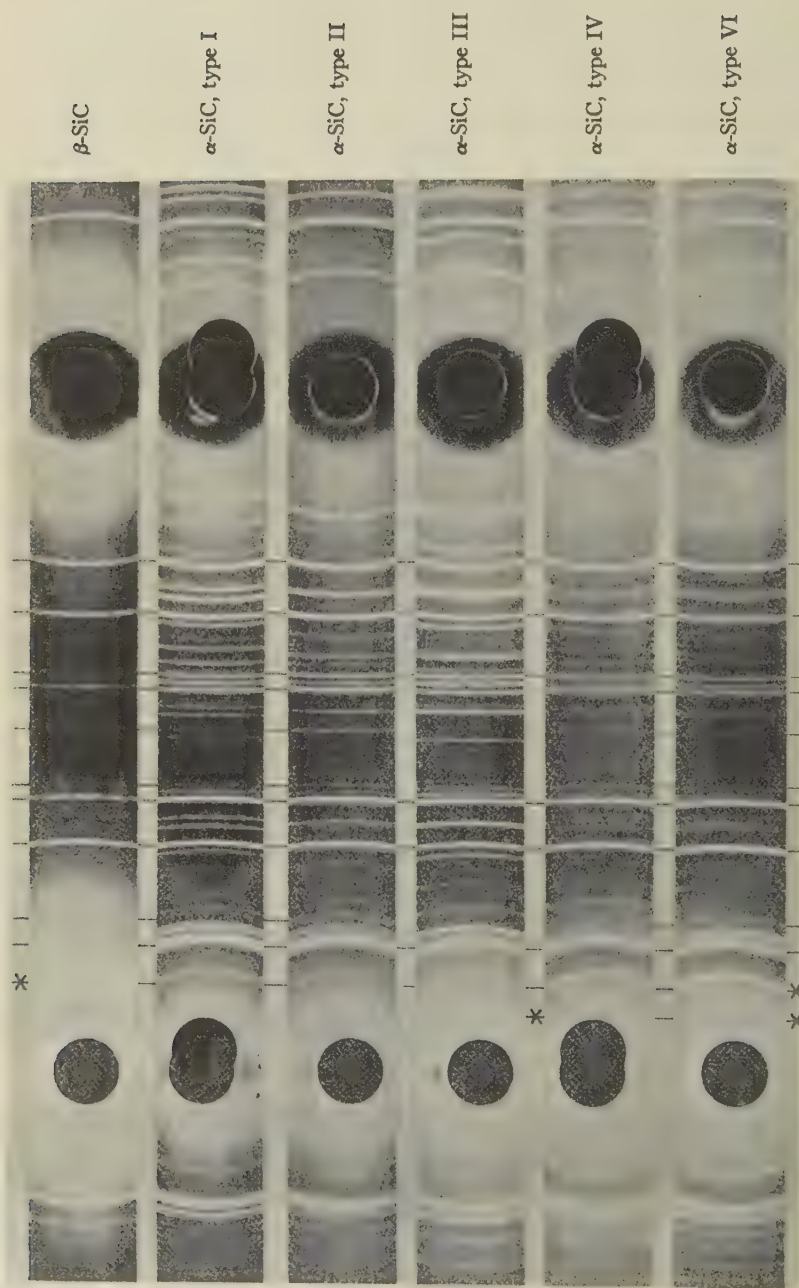


FIG. 12. X-ray Powder Photographs of the SiC Modifications. $\text{CuK}\alpha$ radiation; Camera diameter about 57.3 mm.

Accordingly, all the light green crystals of α -SiC, type II, whose crystal morphology was carefully studied and whose observed axial ratio is recorded in Table 8, were examined under a stereoscopic microscope at a magnification of 30. Those portions containing no visible impurities were segregated, crushed to -200 mesh in a steel mortar, and the magnetic portion removed. To further insure that impurities found in the analysis represented material actually within the SiC itself, either as microscopic or submicroscopic particles or in solid solution, the sample was ignited in an inclined tube furnace at 900°C. for 15 minutes in oxygen to remove any free carbon which might be present. Then it was treated with HF-HNO₃ to remove free SiO₂, free Si, or iron introduced by powdering the sample, should these be present.

Mr. R. M. Rebert, Norton Worcester laboratories, determined the density, d at 30°/4° C. = 3.218, using a 5 cc. pycnometer and xylene as the displacing liquid.

Mr. Rebert then analyzed the sample in duplicate according to the method outlined by Lamar (1939) and obtained:

		<i>Theoretical</i>
Si	69.78%	70.03%
C	29.99	29.97
Al	0.01	
Fe	0.10	
Ca	0.16	
Mg	0.01	
Total	100.05%	

From a portion of the analyzed SiC two powder photographs were prepared, one of the sample itself and another of the sample mixed with an equal portion of highest purity NaCl as a standard. The first indicated that within the limits of the method only type II was present. The second was used for a precise determination of the cell dimensions. a_0 was determined from planes 12.11 and 20.15, both of which gave well-defined doublets of medium to strong intensity in the back reflection position, and the axial ratio, 4.907, obtained from morphological study of the crystals used for the powder photograph and confirmed by equi-inclination Weissenberg photographs. The ratio, 4.907, is certainly correct to within ± 0.001 , and very likely to within ± 0.0005 . The average a_0 value calculated in this manner for type II is 3.073 Å (see Table 24), and the c_0 value obtained by multiplying $a_0 \times c : a$ is 15.07₉ Å (see Table 25). The calculated density is thus 3.217 which compares very favorably with the observed density of 3.218. Siegbahn's wave-lengths, 1940 International

atomic weights and the appropriate value for $1/N$, 1.6503×10^{-24} , were used in the x -ray calculations.

Similarly, from the back reflection planes of the other hexagonal SiC modifications their a_0 value was computed. The $c:a$ ratio used was the ap-

TABLE 24. CELL DIMENSION a_0 OF THE α -SiC MODIFICATIONS CALCULATED FROM THE $d_{hk.l}$ OF BACK REFLECTIONS ON POWDER PHOTOGRAPHS AND THE $c:a$ RATIO OBTAINED FROM MORPHOLOGICAL STUDY

α -SiC type	$hk.l$	$d_{hk.l}$	a_0	a_0 average
I	20.38	.7956	3.074	3.074
	02.37	.8092	3.074	
	12.26	.8271	3.075	
II	20.15	.8021	3.073	3.073
	12.11	.8106	3.072	
III	12.8	.7856	3.074	3.074
	20.10	.8025	3.075	
	12.7	.8236	3.074	
IV	02.55	.7787	3.074	3.073
	20.53	.7973	3.073	
	02.52	.8069	3.073	
VI	20.83	.7993	3.074	3.074
	02.82	.8055	3.074	

TABLE 25. CELL DIMENSIONS, FORMULA WEIGHTS PER CELL AND DENSITIES OF SiC MODIFICATIONS

Modifi- cation	Hexagonal Cell		Rhombohedral Cell		Formula Weights per Hexagonal Cell	Density	
	a_0	c_0	a_r	α		Calc.	Obs.
α -SiC, I	3.073Å	37.70Å	12.69 ₁ Å	13°54 $\frac{1}{2}$ '	15	3.217	—
α -SiC, II	3.073	15.07 ₉	—	—	6	3.217	3.218
α -SiC, III	3.073	10.053	—	—	4	3.217	—
α -SiC, IV	3.073	52.78	17.68 ₃	9°58'	21	3.217	—
α -SiC, VI	3.073	82.94	27.70 ₄	6°21 $\frac{1}{2}$ '	33	3.217	—
<i>Cubic Cell</i>							
β -SiC (Cubic)	$a_0=4.349$		4			3.216	—

appropriate rational multiple of 4.9070 as given in the next to the last column of Table 8 and confirmed by Weissenberg photographs. The results are indicated in Table 24. The a_0 values of all the α -SiC modifications are the same within the limits of error of the method, and 3.073 Å is retained for this dimension. The c_0 values of the other hexagonal modifications are obtained by multiplying 3.073 Å by the appropriate $c:a$ ratio, and are given in Table 25.

The cell dimension of β -SiC was determined from the average value obtained from lines 7–10 inclusive on two powder photographs of the substance. In each case, NaCl was mixed with the cubic SiC to furnish a standard. The calculated density is 3.216, remarkably close to that calculated for the hexagonal modifications.

Relationship of Modifications. It has previously been pointed out that certain planes on and within the crystals were common to two or more of the α -SiC types. Table 26 shows this relationship as derived from powder photographs. As is the case in Table 16, common planes would have the same indices if based on the greatest common divisor c_0 value; this could be obtained by dividing the “ h ” value of the indices of the α -SiC modifications of Table 26 by the number of formula weights per unit hexagonal cell for that modification.

Table 26 and Fig. 12 indicate that except for α -SiC, type III, all the hexagonal varieties contain lines which, within experimental error, are the same as those of β -SiC. This does not indicate, as many have concluded, that cubic SiC is present in the sample, but that all the planes giving powder photograph lines in β -SiC are very closely related to some of the planes of the α -SiC modifications.

The occurrence in the back reflection position of lines from equivalent planes in types II and III provided an excellent opportunity to determine whether the a_0 values of these types were the same and the c_0 values rationally related within the limits of error possible with the powder camera used, as all previous study had led the writer to conclude. A sample of the analyzed (green) type II SiC which was used for the powder photographs was intimately mixed with a sample of black type III whose powder photograph was at hand. As far as could be noted by careful examination of the film resulting from the x -raying of this mixture, all common lines were coincident and the single α_1 line due to both planes 20.10 (type III) and 20.15 (type II) was no broader than that on the photograph of either type alone. In a similar manner, other samples of the analyzed type II powder were mixed with powders of green type I, and with black type II with the same results, namely, that lines due to common planes were always strictly coincident on the photographs.

TABLE 26. X-RAY POWDER PHOTOGRAPH LINES COMMON TO THE SiC MODIFICATIONS

β -SiC <i>hkl</i>	α -SiC types				
	II	III	I	IV	VI
	<i>hkl</i>	<i>hkl</i>	<i>hkl</i>	<i>hkl</i>	<i>hkl</i>
111	{00.6 10.2 10.3	00.4 — 10.2	00.15 01.5 —	00.21 10.7 —	00.33 01.11 —
200	10.4	—	10.10	01.14	10.22
220	{10.8 11.0 10.9	— 11.0 10.6	01.20 11.0 —	10.28 11.0 —	01.44 11.0 —
311	{10.10 11.6 20.2 20.3	— 11.4 — 20.2	10.25 11.15 20.5 —	01.35 11.21 02.7 —	10.55? 11.33 20.11 —
222	{00.12 20.4	— —	00.30 02.10?	00.42 20.14?	00.66 02.22?
400	20.8	—	20.20	02.28	20.44
—	20.9	20.6	—	—	—
331	{10.14 20.10 12.2 12.3	— — — 12.2	01.35 02.25? 12.5 —	10.49 20.35 21.7 —	01.77 02.55 12.11 —
420	{11.12 12.4 10.15	11.8 — 10.10	11.30 21.10? —	11.42 12.14? —	11.66 21.22? —
—	10.16	—	10.40	01.56	10.88
422	{12.8 30.0 12.9	— 30.0 12.6	12.20 30.0 —	21.28 30.0 —	12.44 30.0 —
333}	{00.18 20.14 12.10	00.12 — —	00.45 20.35 21.25	00.63 02.49 12.35	00.99 20.77 21.55?
511}	{30.6 20.15	30.4 20.10	30.15 —	30.21 —	30.33 —

Tone's statement that every lot of hexagonal crystals wherever made will give the same *x*-ray diffraction pattern when examined by the powder method is nearly true in most cases because of the great predominance of type II in all commercial SiC. However, two different varieties of SiC manufactured commercially by the Norton Company give *x*-ray powder diffraction patterns which differ notably in several regions. One variety is a mixture of a large amount of type II and a small amount of type I, while

the other is predominantly type II with a smaller amount of type III.

The x-ray powder pattern of commercial SiC given by Hanawalt and co-workers (1938) and said to be of "cubic and hexagonal forms" is mainly of α -SiC type II with a small amount of type III. There was probably insufficient cubic SiC present to form any pattern. The pattern given by Baumann (1941) as characteristic for SiC contains some of the stronger lines of α -SiC, type II.

EQUI-INCLINATION WEISSENBERG PHOTOGRAPHS

Introduction. Alpha SiC, types I, II, III, IV and VI were studied with the aid of c -axis rotation photographs, and equi-inclination Weissenberg exposures of both c - and a -axis rotations, zero, first and sometimes second layer levels. In the case of β -SiC a zero level of an a -axis rotation, and zero and second layer levels of a dodecahedral axis rotation were made. Obviously not all these exposures were necessary for adequate determinations of the crystal symmetries. Exposures were made with unfiltered copper radiation. The general methods used have been described by Buerger (1942).

Because of the large c_0 cell dimensions of α -SiC, types IV and VI, and the consequent very close spacing of the layer lines of the first kind, rotation photographs were not satisfactory, and it was not always possible to screen out the first from the zero levels in c -axis rotation equi-inclination Weissenberg exposures. These difficulties were of no great consequence, however, because of the information given by a -axis Weissenberg exposures where no such ambiguities existed.

Crystal Classes. Table 27 summarizes the centro-symmetrical crystal classes indicated by plane point-group symmetries shown by the Weissenberg photographs. Actual crystal classes of α -SiC were determined by etching experiments as previously described: types I, IV and VI are $C_{3v}-3m$, and types II and III are $C_{6v}-6mm$. Morphological study of cubic SiC indicated class T_d-43m .

Cell Dimensions. The cell dimensions of all the SiC modifications were determined from the appropriate zero layer Weissenberg photographs, and aided in the precise determination of the lattice constants as discussed under the subject of powder photographs.

Space Groups and Space Lattice Types. The space groups of the various SiC modifications were obtained from characteristic absences noted on indexed Weissenberg photographs. Thus α -SiC, types I, IV and VI are C_{3v}^6-R3m , since:

$(h\bar{k}l)$ is present when $h-k-l=3n$

$(h \cdot h \cdot 2\bar{h} \cdot l)$ is present when $l=3n$

$(h\bar{h}0l)$ is present when $2h-l=3n$.

The space lattice is obviously rhombohedral as was predicted from the morphological study.

TABLE 27. CENTRO-SYMMETRICAL CRYSTAL CLASSES OF THE SiC MODIFICATIONS AS INDICATED BY PLANE POINT-GROUP SYMMETRIES OBTAINED FROM EQUI-INCLINATION WEISSENBERG PHOTOGRAPHS

SiC Modification	Rotation Axis	Level	Plane Symmetry	Centro-Symmetrical Crystal Class
α , types I, IV, VI	c [00.1]	0	C_{61}	D_{3d}
	c [00.1]	1	C_{31}	
	a [11.0]	0	C_2	D_{3d}
	a [11.0]	1	C_2	
α , types II, III	c [00.1]	0	C_{61}	D_{6h}
	c [00.1]	1	C_{61}	
	a [11.0]	0	C_{21}	D_{6h}
	a [11.0]	1	C_{21}	
β	a [100]	0	C_{41}	O_h
	dodecahedral [110]	0	C_{21}	O_h
	dodecahedral [110]	2	C_{21}	

The space group of α -SiC, types II and III is $C_{6v}^4 - C6mc$, since:

- (hkl) is present in all orders
- $(h \cdot h \cdot 2h \cdot l)$ is present when $l=2n$
- $(hh0l)$ is present in all orders.

The space lattice of these types is, therefore, hexagonal as indicated by crystal morphology.

Beta-SiC is $T_d^2 - F\bar{4}3m$ from the following criteria.

- (hkl) present only when $h+k=2n$; $k+l=2n$; $l+h=2n$
- (hhl) present only when $h+l=2n$.

Relationship of Types. In Figs. 13-18 some of the common planes evident from the equi-inclination Weissenberg photographs have been indexed, and may be studied to advantage with the aid of Table 26 which shows most of the correlations to be expected.

The relationship of α -SiC and β -SiC is brought out very clearly in Fig. 18 which is an equi-inclination Weissenberg photograph of the well-developed crystal of β -SiC illustrated by Fig. 9. While this crystal was for the most part β -SiC, there were present within it two thin basal plates of α -SiC whose basal pinacoids were parallel to tetrahedral faces of the β -SiC modification. For the production of the photograph, Fig. 18, the β -SiC crystal was rotated about one of the dodecahedral axes. This was also an

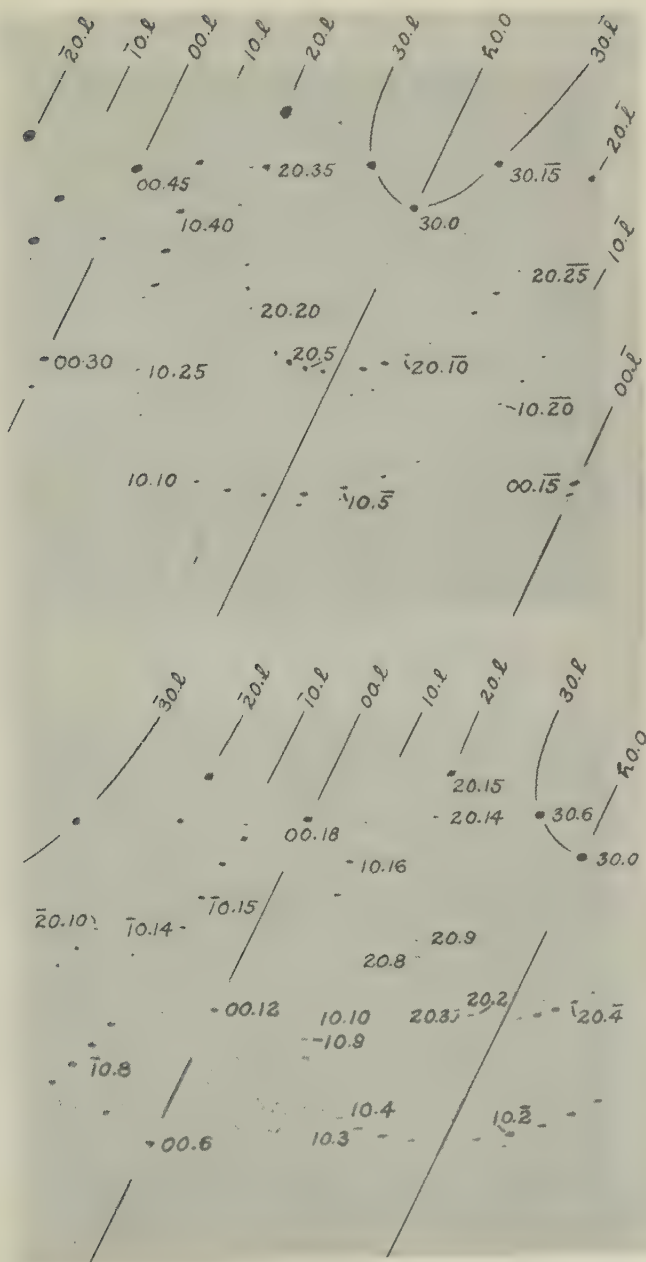


FIG. 13 (upper). Equi-inclination Weissenberg photograph of α -SiC, type I; a -axis rotation, zero level.

FIG. 14 (lower). Equi-inclination Weissenberg photograph of α -SiC, type II; a -axis rotation, zero level.

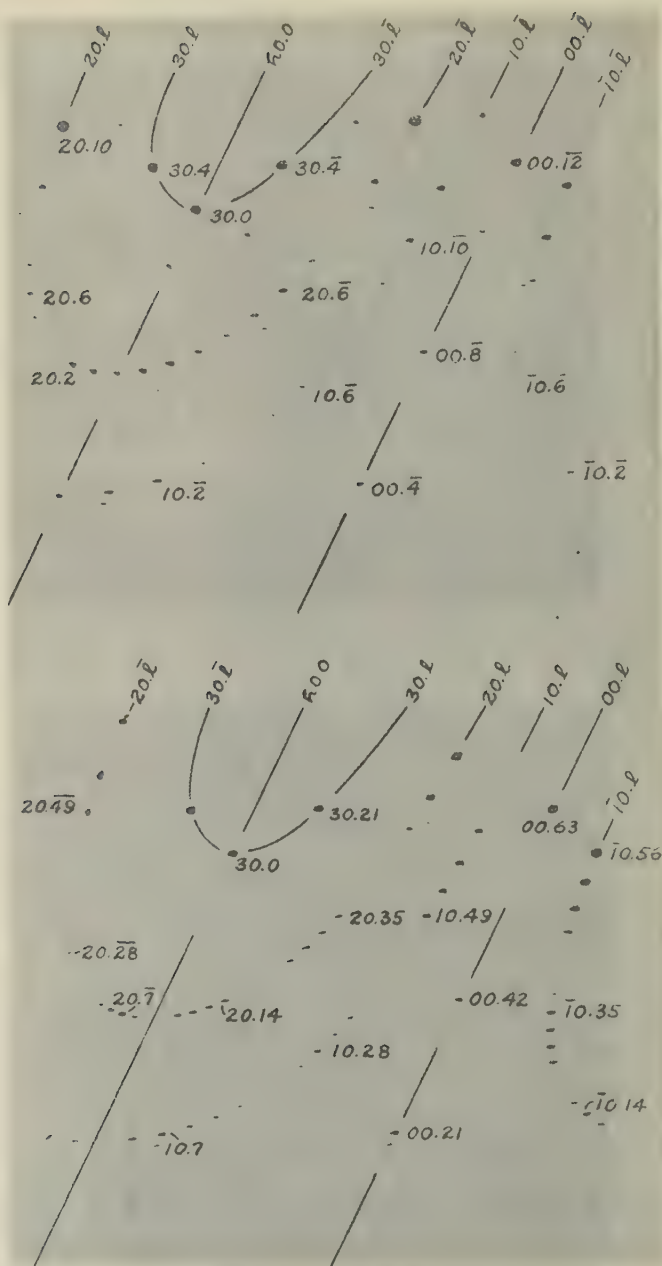


FIG. 15 (upper). Equi-inclination Weissenberg photograph of α -SiC, type III; a -axis rotation, zero level.

FIG. 16 (lower). Equi-inclination Weissenberg photograph of α -SiC, type IV; a -axis rotation, zero level.

α -axis of one of the included α -SiC plates. The resulting Weissenberg photograph was essentially of β -SiC, but with additional faint spots due to an α -axis rotation of α -SiC. These faint spots are very evident on the films in the zone $00\bar{2}$ - $11\bar{1}$ -220. Comparison of this figure with Fig. 14 not only indicates that the included α -SiC plate giving the pattern was type II, but that the following points are exactly coincident.

β -SiC	α -SiC
002	10.4
11 $\bar{1}$	10.2
220	10.8

Although the determination of the ultimate structure of the SiC modifications is beyond the scope of this paper, the data concerning the existing reflections and their intensities as obtained from Weissenberg exposures of α -SiC, types I, II and III during this study are in agreement with those published by Ott. It seems quite certain that the fundamental building block of all the α -SiC modifications is one slightly distorted tetrahedron of SiC, the differences between the types being due to differences in the manner in which these are turned with respect to one another in the direction of the c -axis. All the data are likewise consistent with the sphalerite structure of β -SiC.

OPTICAL PROPERTIES

REVIEW OF LITERATURE

Frazier (1893) stated that SiC was uniaxial.

Becke (1895) obtained a uniaxial positive figure, and observed no pleochroism. The indices of refraction, determined by the Duc de Chaulnes method and measurements on interference figures, were said to be: $\omega_{Na} = 2.786$, $\epsilon_{Na} = 2.832$.

Tone (1908) published curves for the indices of refraction of SiC for various wave-lengths, the indices apparently having been calculated from interference phenomena. For sodium light the values obtained from the curves were approximately: $\omega = 2.83$, $\epsilon = 2.98$. SiC was said to be more transparent perpendicular to the c -axis than parallel to it.

Pirsson (1914) stated that SiC was uniaxial positive with weak double refraction, and that the indices for both rays were greater than 1.75. He observed some pleochroism: ϵ = deep indigo blue; ω = light blue.

Merwin (1917) determined the indices of refraction of the o ray for various wave-lengths by using the method of minimum deviation on two naturally occurring prisms found on a very pale green crystal of SiC, one face on each prism being somewhat curved. The values for the e ray were

obtained by measurements on the interference figure according to the method of Merwin (1914). The values for sodium light were: $\omega = 2.654$, $\epsilon = 2.697$. Merwin observed that bluish SiC was pleochroic light to dark blue, or olive green to greenish blue, but stated that the σ ray was the more strongly absorbed.

Somewhat earlier Weigel (1916) published a paper including detailed observations on the indices of refraction of SiC for various wave-lengths and also for higher temperatures. For these purposes three prisms were very accurately ground and polished so that their refracting edges were parallel to the crystallographic c -axis. Two of the prisms were of clear, presumably light green, SiC, while the third was cut from black SiC. No determinations were made with sodium light, but interpolation gives: $\omega_{Na} = 2.6477$, $\epsilon_{Na} = 2.6934$ at about 22°C. Within experimental error, the values obtained on the black crystal were the same as those for the green crystals, so Weigel concluded that the impurity causing the color was admixed mechanically and did not exist in solid solution.

Many English-language reference texts, including Winchell (1931), Larsen and Berman (1934), and the *Handbook of Chemistry and Physics* (1943) quote Merwin's values for the indices of refraction. The *International Critical Tables* (1926) and Mellor (1924) give the values determined both by Merwin and Weigel. Winchell gives as the pleochroism formula: $X(\omega) > Z(\epsilon)$ while Larsen and Berman state: $\omega = \text{light blue}$; $\epsilon = \text{deep indigo blue}$, which would be equivalent to $Z > X$.

No optical data on cubic SiC have appeared in the literature.

ALPHA SILICON CARBIDE

Examination in Polarized Light. The normal interference figure of all the hexagonal SiC types throughout the visible spectrum is uniaxial positive. However, biaxiality due to strain, with 2V up to about 10°, may sometimes be observed, especially adjacent to opaque inclusions. Crystals of types I and II were examined for biaxiality but there was no evidence that it occurred more in one type than in the other.

Several pale green crystals of both types I and II up to 2 mm. in thickness were examined for optical activity in lithium, and mercury yellow, green and blue light, but there was no evidence of the rotation of the plane of polarization, nor was the interference figure that of an optically active crystal.

Color and Dichroism. Hexagonal SiC crystals are yellow, greenish-yellow, green, blue green, blue, gray, or black, the particular shade depending considerably upon the conditions of illumination, the size of the individuals and sometimes on the direction of view into the crystal. When

crushed to a fine size and observed by transmitted light, even the darkest silicon carbide will usually transmit some light and appear blue. Extremely pale green, almost colorless, crystals up to a millimeter in thickness have been found, but red SiC as reported by Winchell (1931) has not been observed by the writer. Crystals often show considerable color variation which may be irregular or zonal in nature.

The correlation between color and α -SiC type which Frazier, Baumhauer, and Espig have described was only partially substantiated. In a small sample of green crude forwarded by a foreign manufacturer there was apparently a perfect correlation between color and type, for in over 40 crystals measured from this specimen all the greenish yellow crystals were type I and all the green or blue green, type II. Moreover, when coalescences occurred, there was a sharp line of demarcation in color at the boundary between types, even when a thin plate of type I occurred between larger masses of type II. Each type was also characterized by its own dichroism as indicated by specimens 1*a* and 1*b* in Table 28.

TABLE 28. COLOR, DICHROISM AND ABSORPTION OF ALPHA SILICON CARBIDE TYPES

No.	SiC Type	Color of Crystal	Dichroism	Absorption	Remarks
1 <i>a</i>	I	greenish yellow	ϵ = light greenish blue	$\epsilon > \omega?$	Coalescence of types I & II
1 <i>b</i>	II	blue green	ω = light lemon yellow ϵ = medium blue green ω = light green		
2 <i>a</i>	I	greenish yellow	ω = greenish blue ω = lemon yellow	$\epsilon > \omega?$	Different parts of same crystal, same type
2 <i>b</i>	I	blue streak in above	ϵ = pale gray blue ω = gray blue	$\omega > \epsilon$	
3 <i>a</i>	I	greenish yellow	ϵ = light greenish blue ω = light olive green	?	Coalescence of types I & II
3 <i>b</i>	II	light blue	ϵ = light blue ω = very pale blue		
4 <i>a</i>	I	green	ϵ = medium greenish blue ω = light green	$\epsilon > \omega$	Different parts of same crystal, same type
4 <i>b</i>	I	blue streaks in above	ϵ = light gray blue ω = indigo blue		

TABLE 28—Continued

No.	SiC type	Color of Crystal	Dichroism	Absorption	Remarks
4c	II		same as 4a	$\epsilon > \omega$	4a and 4b (type I) coalesced with 4c and 4d (type II)
4d	II		same as 4b	$\omega > \epsilon$	
5	I	light yellow green	ϵ =light green ω =light buff	$\epsilon > \omega$	
6	I	blue black	ϵ =blue ω =very dark blue	$\omega > \epsilon$	
7	II	bluish green	ϵ =light blue ω =light blue green	?	
8	II	green	ϵ =blue green ω =yellow green	$\epsilon > \omega$	
9	II	light blue	ϵ =light blue ω =almost colorless	$\epsilon > \omega$	
10	II	dark blue	ϵ =light blue ω =dark blue	$\omega > \epsilon$	
11	II	black	ϵ =medium blue ω =very dark blue	$\omega > \epsilon$	From same small crude specimen
12	III	black	ϵ =medium blue ω =very dark blue	$\omega > \epsilon$	
13	IV	greenish yellow	ϵ =very pale green ω =very pale olive	$\epsilon > \omega?$	
14	VI	blue black	ϵ =medium blue ω =dark blue	$\omega > \epsilon$	
15	n.d.	blue	ϵ =pale purplish blue ω =medium blue	$\omega > \epsilon$	

A somewhat larger specimen of green SiC crude supplied by another foreign producer contained no greenish yellow or yellow crystals. Examination of over 60 crystals from this sample revealed that while most of the individuals were type II, there were a few of type I and a few coalescences. Specimens 4a, b, c, d, Table 28, are from this lot. It is to be noted

that there was no difference in color nor in dichroism between the type I and type II portions of this coalescence.

Because of the disagreement in the literature concerning the dichroism and especially the absorption formula for silicon carbide, a complete study of these properties for each of the hexagonal types was undertaken. The difficulty of obtaining satisfactory transmission of light through irregular fragments even when immersed in methylene iodide made it advisable to cut thin plates from the crystals parallel to the c axis with the aid of a suitable diamond cut-off wheel. Table 28 correlates the color, dichroism and absorption found for various crystals of the different α -SiC types.

The reason for the disagreement in the literature concerning the dichroism and absorption of hexagonal SiC no doubt is due to the variation in these properties in crystals from the same or different sources, variations which are probably caused by differences in accompanying impurities.

Indices of Refraction and Dispersion. Although the relationship between the different modifications of α -SiC clearly indicates that no differences in indices of refraction due to the structural differences between types are to be expected, it was nevertheless thought worth while to determine the indices of refraction and dispersion of two different α -SiC types. The purpose was three-fold: (1) to check the values published by Weigel and Merwin, (2) to determine experimentally whether different types were characterized by different refractive indices, and (3) to ascertain whether there were differences in indices due to material in solid solution or submicroscopic suspension in the crystal.

Prisms suitable for refractive index determinations were prepared in the following manner. A thick tabular crystal containing one large well-developed basal pinacoid was cemented to a suitable block of plate glass, the base of the crystal being in contact with the glass surface. Two cuts were then made through the crystal and into the glass with a diamond cut-off wheel such that a prism of about 40° was formed, the cut surfaces being essentially perpendicular to the basal pinacoid, and the prism edge, therefore, nearly parallel to the c -axis. For this operation the author is indebted to Dr. J. E. Burke, Norton Worcester laboratories. Each of the prism faces was polished by successively mounting in phenol formaldehyde plastic and polishing with 2 micron diamond on a lead lap, using the Graton-Vanderwilt polishing machine. The signals reflected from the prism faces on the goniometer were single, undistorted and perfectly sharp.

Three prisms were prepared in the above manner. Prism No. 1 was cut from a transparent, light green crystal of type II. It was free from flaws

and exhibited the dichroism, ϵ =medium greenish blue, ω =light green. Prism No. 2 was prepared from the same coalescence of types I and II as the plate whose dichroism is described in Table 28, specimens 1a and 1b. The purpose of cutting a prism from a coalescence was to permit a greater degree of precision in comparing the indices of refraction of the two types. If the indices of the types differed even slightly, it would be evident immediately when the minimum deviation angle was measured in monochromatic light, since four signals would be observed through the telescope of the goniometer, two from each type. This was found to be the case with prism No. 2 as is indicated by the values for the indices of refraction given in Table 29. Prism No. 3 was obtained from a green crystal of type I which varied greatly in color, and for this reason all but about one square millimeter of each prism surface was blocked off with opaque ink. The portion of prism No. 3 used to determine the indices of refraction showed the same dichroism as prism No. 1. Its identity as type I was checked by an x-ray powder photograph of the portion used for the optical examinations.

Each prism was set up on the same goniometer used for the morphological study. The prism angle was measured ten times on different parts of the scale, the average being used in the calculations. The minimum deviation angles for the ordinary and extraordinary rays through the prism were measured three times for each of the wave-lengths of light used. Finally the angle between each polished prism face and the basal pinacoid was measured five times, these measurements being necessary to determine the true ϵ value.

Omega and ϵ' were determined from the prism angles and the deviation angles by the usual formula for minimum deviation. The results appear under the columns headed " ω , 1st" and " ϵ' 1st" in Table 29. Subsequently, the prism and deviation angles were measured again, the results of these calculations appearing under the columns headed "2nd." Monochromatic light was supplied by a mercury vapor tube, hydrogen Geissler tube and sodium and lithium flames. The most precise measurements of indices of refraction given in Table 29 are indicated by asterisks. The absence of a symbol indicates average precision while less reliability is indicated by question marks. The reason for the latter was the weak signals, and therefore, somewhat uncertain deviation angles, afforded by some of the prisms for some of the wave-lengths. It is believed that the average values indicated by asterisks are correct to within ± 0.0003 .

The prisms were cut in such a manner that the refracting edges were approximately parallel to the c -axis. However, because of the methods employed, high precision could not be attained, and for that reason the index obtained for the extraordinary ray by the usual formula was the

TABLE 29. INDICES OF REFRACTION AND DISPERSION OF α -SiC, TYPES I AND II

Wave Length (Å)	Prism No. & SiC Type	ω			ϵ'			ϵ (calc.)
		1st	2nd	Avg.	1st	2nd	Avg.	
6708 (Li)	1, II	2.6264	2.6267	2.6266	2.6676??	2.6671??	2.6674??	2.6674??
	2a, I	—	—	—	—	—	—	—
	2b, II	—	—	—	—	—	—	—
	3, I	2.6269	2.6265	2.6267	—	—	—	—
6563 (H)	1, II	2.6294*	2.6297*	2.6296*	2.6696	2.6695	2.6696	2.6696
	2a, I	2.6283	2.6285	2.6284	—	—	—	—
	2b, II	2.6307	2.6309	2.6308	—	—	—	—
	3, I	2.6294*	2.6288*	2.6291*	2.6700?	2.6692?	2.6696?	2.6697?
5895 (Na)	1, II	2.6474*	2.6476*	2.6475*	2.6889*	2.6888*	2.6889*	2.6889*
	2a, I	2.6465	2.6469	2.6467	2.6923	2.6928	2.6926	2.6930
	2b, II	2.6485	2.6489	2.6487	2.6905	2.6904	2.6905	2.6909
	3, I	2.6470*	2.6466*	2.6468*	2.6891*	2.6890*	2.6891*	2.6892*
5781 (Hg)	1, II	2.6509*	2.6513*	2.6511*	2.6931*	2.6934*	2.6933*	2.6933*
	2a, I	2.6502*	2.6505*	2.6504*	2.6963	2.6966	2.6965	2.6969
	2b, II	2.6522*	2.6527*	2.6525*	2.6946	2.6947	2.6947	2.6951
	3, I	2.6506*	2.6505*	2.6506*	2.6930*	2.6930*	2.6930*	2.6931*
5461 (Hg)	1, II	2.6629*	2.6632*	2.6631*	2.7062*	2.7065*	2.7064*	2.7064*
	2a, I	2.6622*	2.6624*	2.6623*	2.7094	2.7096	2.7095	2.7099
	2b, II	2.6640*	2.6644*	2.6642*	2.7071	2.7073	2.7072	2.7076
	3, I	2.6625*	2.6624*	2.6625*	2.7059*	2.7065*	2.7062*	2.7063*
4867 (H)	1, II	2.6923	2.6932	2.6928	2.7410??	2.7421??	2.7416??	2.7416??
	2a, I	2.6920	2.6918	2.6919	—	—	—	—
	2b, II	2.6941	2.6945	2.6943	—	—	—	—
	3, I	2.6931	2.6923	2.6927	2.7398?	2.7409?	2.7404?	2.7405?
4358 (Hg)	1, II	2.7304	2.7305	2.7305	2.7825	2.7822	2.7824	2.7824
	2a, I	2.7298	2.7302	2.7300	2.7852?	2.7860?	2.7856?	2.7860?
	2b, II	2.7319	2.7321	2.7320	2.7835?	2.7830?	2.7833?	2.7837?
	3, I	2.7301	2.7294	2.7298	2.7818	2.7822	2.7820	2.7821
4047 (Hg)	1, II	2.7652?	2.7650?	2.7651?	—	—	—	—
	2a, I	—	—	—	—	—	—	—
	2b, II	—	—	—	—	—	—	—
	3, I	2.7635?	2.7640?	2.7638?	—	—	—	—

apparent value (ϵ') and not necessarily the true value (ϵ). The latter may be calculated from the true prism angle and the angle which each of the

prism faces makes with the basal pinacoid by the use of a series equations given by Born (1887). The writer is indebted to Mr. K. F. Whitcomb, Norton Worcester laboratories for some of the necessary calculations based on solid analytical geometry. Table 29, however, indicates that the maximum difference between ϵ' and ϵ hardly exceeds the experimental error of the best measurements of ϵ' .

Types I and II α -SiC are not characterized by different refractive indices since both ω and ϵ of prism No. 1 (type II) and prism No. 3 (type I) are the same within experimental error. From this we may conclude that the indices of refraction of all α -SiC types are fundamentally the same.

In disagreement with the conclusions of Weigel, however, differences in indices of refraction, presumably due to material in solid solution in the crystal, do occur within a single type as indicated by the differences found between the values obtained from prisms No. 1 and No. 2*b*, type II, or from prisms No. 2*a* and No. 3 both type I.

Additional proof of the influence of material in solid solution on the indices of refraction of α -SiC was afforded by prism No. 3. Although the polished prism surfaces reflected faultless signals on the goniometer, multiple signals accompanied by blurs were observed for both the ordinary and extraordinary rays passing through the prism. No indication of any biaxiality could be observed, so it seems improbable that the multiple signals were due to strains in the crystal. A marked variation in color was observed under the microscope. One area about 1 mm. square was uniformly light green, while the remainder of the prism varied from light green to medium blue. By permitting light to pass only through small portions of the prism at a time, it was found that the differently colored zones gave ordinary and extraordinary ray signals which varied slightly in position. This indicated differences in indices of refraction with color, which must be caused by variation in the amount or kind of material in solid solution or submicroscopic suspension. The indices given in Table 29 for this prism were obtained from the light green area which gave minimum values. The indices from the darker areas could not be determined satisfactorily but in some cases were certainly higher by at least 0.002.

Table 29 indicates that the following variations in indices for Na-light have been observed during the present study:

$$\omega = 2.6467\text{--}2.6487$$

$$\epsilon = 2.6889\text{--}2.6930$$

Similar variations were found for all other wave-lengths so that the dispersions of both ω and ϵ were the same for all prisms, the average values being:

$$\text{Dispersion of } \omega \text{ (4360--6200 } \text{\AA}) = 0.0918$$

$$\text{Dispersion of } \epsilon \text{ (4360--6200 } \text{\AA}) = 0.1028.$$

The data on the indices of refraction of SiC published by Becke (1895) and Tone (1908) are incorrect, since the methods used by them for the determination of the optical constants are not accurate. All of the indices of refraction determined during the course of the present study were 0.005 to 0.009 lower than the values given by Merwin for corresponding wave-lengths. This is probably due to inaccuracies resulting from the curved surfaces on Merwin's prism faces. The indices of refraction of the ordinary ray for all the prisms studied were within about 0.001 of the values given by Weigel (1916) for all wave-lengths. The ϵ of prism 2a was within 0.0006 of Weigel's determinations for all wave-lengths, but the same values from the other prisms were 0.003 to 0.004 lower than reported by him. The dispersions agreed with the values reported by Weigel.

BETA SILICON CARBIDE

The cubic SiC encountered in the course of this study was transparent, yellow to olive green in color, and for the most part isotropic. In practically all cases, however, lamellae of an anisotropic substance were present as inclusions.

A study of β -SiC was made by embedding fragments of it in sulphur-selenium melts of known indices of refraction using fragments of a green crystal of α -SiC, type II, as control. The wave-length used was essentially equivalent to that of lithium because of the high index of the melts found necessary. The index of β -SiC for this wave-length is close to 2.63, about that of the o ray of α -SiC.

Petrographic examination of the cubic SiC crystal illustrated by Fig. 9 indicated that the anisotropic substance included within it was in the form of very thin basal plates parallel to tetrahedron faces of the β -SiC. These plates were found to be uniaxial positive with ω for Li about 2.63 and $\epsilon > 2.66$. These facts, together with similar spatial relationships found between crystals of β -SiC and macroscopic crystals of α -SiC, indicate that the lamellae are basal plates of α -SiC, confirming a conclusion already reached from x -ray studies.

OTHER POLYTYPIC SUBSTANCES

SiC was for a number of years the only known substance exhibiting the phenomenon of polytypism, and may today be considered the prototype of polytypic compounds because of the large number of types and the detail in which they have been studied. In recent years, however, data have appeared which clearly indicate that several other compounds are polytypic. For the most part the following descriptions have been taken from the literature.

Coquimbite and paracoquimbite, both with the formula $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 9\text{H}_2\text{O}$, are two minerals, which have been described as polytypic by Ungemach (1935*a*) and confirmed by Bandy (1938). The series of crystal forms of coquimbite is characteristic of a hexagonal substance while that of paracoquimbite is characteristic of a rhombohedral lattice. When the indices of the forms are simplified to the greatest extent, the indicated $c:a$ ratios are 1.5643 and 4.6928 respectively, the values being exactly rationally related as 1:3.

Rotation photographs of the two substances yielded the following cell dimensions, both being referred to the smallest hexagonal unit:

	<i>Coquimbite</i>	<i>Paracoquimbite</i>
a_0	10.8 ₅ Å	10.90 Å
c_0	17.0 ₃ Å	51.1 ₅ Å

Thus the a_0 values are probably the same, and the c_0 dimensions rationally related within the limit of error of the measurements.

Syntactic intergrowths of coquimbite and paracoquimbite are very common, several examples of which are adequately illustrated by Ungemach's crystal drawings. The plane of contact between the individuals involved in the coalescences is always the basal pinacoid, the line of demarcation often being evident on the crystal by re-entrant angles or striations.

The similarity of the morphological and structural crystallography of coquimbite and paracoquimbite to that of the α -SiC types is so evident that no comments need be made.

In a paper on syntaxis and polytypism Ungemach (1935*b*) has shown that the minerals parisite and synchisite may very reasonably be divided into three modifications or types, all having the same composition $(\text{CeF})_2\text{Ca}(\text{CO}_3)_3$. The crystals of these minerals are not as well developed as are those of SiC or coquimbite-paracoquimbite, but it seemed possible to establish the three varieties with the following $c:a$ ratios:

α -parisite (hexagonal)	= 4.473
β -parisite (rhombohedral)	= 10.094
γ -parisite (hexagonal)	= 6.730

These three axial ratios are rationally related as 4:9:6. Again certain crystal forms are common to two or all three of the varieties which often form syntactic intergrowths (coalescences).

For a number of years the x -ray powder photographs of several samples of natural graphites have been observed to show "extra" lines, apparently not due to impurities, but not indexed on the basis of the known graphite structure. Lipson and Stokes (1942*a*, 1942*b*) find that these lines may be accounted for on the assumption that there exists within these

samples about 14% of another form of graphite whose a_0 cell dimension is the same as that of ordinary graphite, but whose c_0 value is $3/2$ as great. This new structure is said to be based on a rhombohedral lattice and to belong to space group $R\bar{3}m$ whereas ordinary graphite is based on a hexagonal cell and belongs to $C6mc$. Again these appear to be polytypic compounds.

It seems quite certain that as more complete morphological and structural data concerning both minerals and artificial compounds become available, more polytypic substances will be found. The most fruitful field of search would seem to be compounds crystallizing in the hexagonal system, where polytypism might explain the appearance of two or more incompatible series of crystal forms, for example, a rhombohedral and a holohedral series, inconsistent x -ray patterns, or data seemingly showing transitions, etc. The crystal systems of lower symmetry should not be overlooked, however. The value of the optical goniometer in connection with the study of polytypic substances cannot be overemphasized, for the study of SiC has amply proven the rapidity and certainty with which the various types and the presence of syntactic intergrowths or coalescences may be determined with its aid. Entirely incorrect or inexplicable data might well result from the x -ray examination, without adequate morphological study, of a crystal which appeared to be single and well developed, but which actually was a syntactic intergrowth of two or more types.

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THE COMPOSITION AND STRUCTURE OF MINNESOTAITE, A COMMON IRON SILICATE IN IRON FORMATIONS*

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ABSTRACT

The identity of a very abundant iron silicate in the iron formations of Minnesota has been established as an iron talc. Its structure and properties have been investigated and compared with its two associated silicates, stilpnomelane and greenalite.

INTRODUCTION

Ever since the discovery of the productive portion of the Mesabi range—the part west of the railroad from Two Harbors to Tower—petrographers have observed a mineral in this part of the Biwabik iron formation which they called an amphibole (1 and 2). This mineral, sometimes designated more specifically as grunerite, is *not* an amphibole but a talc. Grunerite and other amphiboles are found *only* on the East Mesabi range, that is, east of the railroad mentioned above. The mineral under consideration is very abundant in certain horizons of the Biwabik formation. These horizons have been mapped as “Slaty Divisions” by Wolff and Gruner (3). The mineral occurs, however, also in the “Cherty Divisions.” In either case the rocks containing it in abundance have been called in the past, for the sake of classification, greenalite taconite and slaty taconite, and sometimes just greenalite rock.

It is proposed that this mineral be called *minnesotaite* because it was discovered in Minnesota and probably is more abundant in this state than anywhere else. It is also found on the Cuyuna range in central Minnesota. The minerals most commonly associated with minnesotaite are quartz, siderite, stilpnomelane, greenalite, and magnetite. Any two or three, or all five, may be found together. Stilpnomelane has not previously been reported in thin sections from the Mesabi range. It was discovered in x-ray powder photographs and then found under the microscope. Although abundant, it is very fine grained and hidden in the dense dark portions of the slaty taconite. Greenalite, in small amounts, is often found with minnesotaite. In a few places the two may be equally abundant. Siderite may be present in considerable quantities as the rock contains from 5% to as much as 15% of CO₂. Quartz, usually called chert, varies from practically nothing to 90% in volume.

Minnesotaite occurs only in microscopic plates or needles, the latter radiated or in sheaves. Sometimes it is so abundant that an inch of a drill

* A part of an investigation of the taconites of the Mesabi Range by the Iron Range Resources and Rehabilitation Commission of Minnesota.

core may contain up to 90% of it, the rest being the other minerals mentioned.

The first investigator who positively stated that this "amphibole" was not an amphibole was Richarz (4, p. 701). He showed that the mineral had parallel extinction in all positions and, therefore, being an iron silicate, could not be an amphibole. He mentioned its similarity to mica and for want of a better name suggested "crystallized greenalite."

In 1935 Jolliffe (5) described the optical properties and even made a partial chemical analysis of it, though, as will be shown below, he did not have the choicest material. He called the material "mineral X." As Jolliffe did not employ x-rays in his studies he was unaware of the fact that he was dealing with three distinctly different silicates; namely, greenalite, stilpnomelane, and minnesotaite. He called them greenalite, metagreenalite (supposedly like greenalite in composition), and mineral X. The formula he proposed for greenalite is similar to that of minnesotaite and is quite different from true greenalite, which is an iron serpentine as shown by the writer (6) in 1936.

The author is indebted for aid and many suggestions in this study to Dr. R. B. Ellestad and Mr. Lynn Gardiner. The Graduate School of the University of Minnesota supported the work with generous grants.

OPTICAL DATA

It is not intended to give a detailed description of the occurrence of minnesotaite at this time, since it occurs not only on the Mesabi but also on the Cuyuna range and probably will be found in other iron formations. Neither will its derivation from any of the other minerals be discussed at present. Such a study has not been completed. The descriptions of earlier mineralogists agree as to its occurrence and relationship to the associated minerals (1, 2, 4, and 5). It is fibrous, rarely platy, in appearance and reminds one of sericite or pyrophyllite in thin sections. In the hand specimen it has a greenish-gray color. Usually, though not always, it is lighter than greenalite, which is a dark olive green. It is so soft that it is easily scratched by a mounted steel needle drawn across it under the weight of the metallic needle mounting. The coarsest grained material looks greasy to waxy under binoculars. The finer grained material is waxy to dull in luster. The optical properties would not be expected to be very constant for a mineral in which the amounts Fe²⁺, Fe³⁺, and Mg are somewhat variable.

The mineral has parallel extinction, a small optic angle with the acute bisectrix normal to the basal cleavage, and fairly high birefringence. Jolliffe's figures (5, p. 412) have been confirmed for the colorless variety and

differ little from those of Richarz (4, p. 701). $N_\gamma - N_\alpha = 1.615 - 1.580 = 0.035$. Positive elongation. Many specimens show practically no pleochroism but it may become noticeable and then Z and Y = pale green, X = colorless, or very pale yellow. In some sections the larger colorless needles will grade into definitely light yellowish-green confused aggregates of very small fibers. It was thought at first that these aggregates might be a different mineral but the x -rays show that they are also minnesotaite. The fibers are noticeably pleochroic and form ill-defined areas resembling somewhat the shape and size of greenalite granules. Associated stilpnomelane was not recognized as such by former investigators, chiefly because it is in such fine-grained aggregates in most sections that its strong pleochroism and parallel extinction are difficult to see.

It is possible that Jolliffe included it under his "metagreenalite." Most of the material which he (5, p. 411) designated as such is minnesotaite. It is so fine grained that even with a magnification of 300 diameters the material appears as felt-like yellowish-green masses. When these aggregates occur as granules they differ from greenalite only by their mottled appearance between crossed nicols. They were definitely identified as minnesotaite by using x -rays. They seem to have somewhat higher indices of refraction than the lighter colored, coarser minnesotaite described above and may contain more ferric iron. Here we have the unusual situation of two apparently different substances being alike in structure and probably very similar, if not identical, in composition.

X-RAY DATA

When greenalite was first x -rayed by the writer in 1934 (6), it happened that the material contained neither minnesotaite nor stilpnomelane in sufficient amounts to give their characteristic patterns. When a new study of the iron formations of Minnesota was begun in 1941, almost the first x -ray powder photograph showed patterns of both these minerals in association with quartz and iron carbonate. It is relatively easy to remove the carbonate without injury to the silicates, since the carbonate is soluble in boiling HCl. The finely powdered specimen is heated in about 200 cc. of nearly boiling water and to it is added a little more HCl than is estimated to dissolve the carbonate. Effervescence is very vigorous for a short time. As soon as it stops the solution is diluted to twice its volume with cold water. The powder that settles is washed by repeated decantation. It is practically impossible to separate stilpnomelane from minnesotaite. They are so similar in densities and other properties that no known method will produce results. It is, however, feasible to extract greenalite dielectrically. Most quartz can be removed relatively easily by centrifug-

ing in bromoform, except in the presence of stilpnomelane. Magnetite is removed by a hand magnet. A powerful electromagnet will also attract minnesotaite, stilpnomelane, and greenalite.

The most suitable material for x -ray and chemical analysis was a piece of drill core from a depth of 240 feet (M 4450) which contained practically no quartz, very little carbonate, but some magnetite. A powder was prepared which showed no trace of quartz in the x -ray powder photographs.

Its x -ray spacings are given in Table 1 in comparison with those of talc (9, p. 416) and margarite. Of the latter two minerals only those lines are listed which could be correlated with minnesotaite. They are mostly basal

TABLE 1. COMPARISON OF X-RAY PHOTOGRAPHS UNFILTERED Fe RADIATION.
CAMERA RADIUS=57.3 MM.

No.	Minnesotaite ¹		Talc (9, p. 416)		Margarite ²		Indices
	d	I	d	I	d	I	
1	9.53	10+	9.26	5	9.47	1-2	002
2	4.77	1	4.63	3	4.72	0.5	004
3	3.50	1	3.39	2	3.51	3	006 β
4	3.177	5	3.086	10	3.168	10	006
5	2.750	0.5 b			2.769	2	
6	2.651	0.5	2.578	1	2.677	1	
7	2.524	2	2.462	5	2.522	2 b	
8	2.397	1			2.402	2	
9			2.315	1			008
10	2.312	0.5					
11	2.215	1					
12	2.112	0.5	2.039	1	2.097	1	0010 β
13	2.005	1					
14	1.917	1	1.852	3	1.902	5	0010
15	1.659	1					
16	1.598	1 b	1.544	2	1.608	2	0012
17	1.567	1	1.517	4	?		060
18	1.514	0.5					
19	1.384	0.5 b					
20	1.366	1	1.323	1	1.361	0.5	0014
21	1.352	1	1.294	2	1.294	1	
22	1.329	1					
23	1.198	faint					
24			1.160	0.5			0016
25	1.177	0.5					

¹ Mesabi Range, No. 4450, Depth—240 feet.

² Emery Mines, Chester, Mass.

reflections. It is doubtful if line No. 16 of minnesotaite, which is broad, originates from 0012, though part of the reflection may be caused by it. The same may be said of line No. 12.

The similarity of the three photographs except for the intensities of 002, 004, 006, 0010, and 0012 is unmistakable. On the assumption that minnesotaite has a talc structure the theoretical intensities of the basal

TABLE 2. THEORETICAL AND OBSERVED INTENSITIES OF BASAL PLANES OF MINNESOTAITE

Indices	002	004	006	008	0010	0012	0014	0016
Spacing	9.550	4.775	3.183	2.387	1.910	1.592	1.364	1.194
Observed Intensity	10+	1	5	0	1	?	1	?
Theoretical Intensity	120	0.5	22	0	0.7	0.2	1	0.1

reflections were computed and are compared with the observed ones in Table 2. The agreement may be called fair, considering the assumptions which must be made with regard to the scattering factors. The ratio of Fe to Mg ions in the octahedral layer of the structure was taken as 3 to 1 in the calculation of the scattering factors. Disregarding the angle β (provided the mineral is monoclinic) we have a unit cell with the following dimensions:

$$d_{001} = 19.10 \text{ \AA}, b_0 = 9.40 \text{ \AA}, a_0 = 5.4 \text{ \AA}$$

The length of a_0 is based on the pseudo-hexagonal character of the structure.

The dimension 19.10 Å for 001 is somewhat larger than one would expect when compared with $18.58 \pm .03$ Å for magnesium talc from Harford County, Maryland. On the other hand, 001 for margarite is very similar to minnesotaite. One is tempted, therefore, to consider the possibility of a "brittle iron mica" structure in which Fe⁺⁺ takes the place of K or Ca, respectively. The writer is not thinking of such minerals as chloritoid or ottrelite, which do not belong here structurally, but of a regular mica structure. It is at once realized that the chemical composition given below does not fulfill the requirements for such a mica. The structure would have to be a defect structure with a considerable number of positions where Fe is missing. The ratio of vacancies to the filled positions between the layers would be nearly 7 to 1. There are other complications that would arise in such a scheme as, for example, density, hardness, and opti-

cal discrepancies. On the other hand, the theoretical reflections from the basal planes would agree somewhat better than those of Table 2.

CHEMICAL DATA

Jolliffe (5, p. 416) made an attempt in 1935 to analyze minnesotaite. He does not mention how large a sample he had but states that he corrected the analysis for impurities. His results recalculated by the writer are recorded in columns 6 and 7 of Table 3. Dr. R. B. Ellestad made an analysis of the purified mineral whose x -ray pattern is given in Table 1. About 7 grams of material for a regular mineral analysis were available. TiO_2 and P_2O_5 were not determined because from thousands of analyses we know that these constituents are present in very minor amounts in the iron formations. There is a little MnO present which is included in the

TABLE 3. ANALYSES, ATOMIC DISTRIBUTION, AND DENSITIES OF MINNESOTAITE

Minnesotaite, R. B. Ellestad, <i>Analyst</i>						Jolliffe's Mineral "X"	
	1	2	3	4	5	6	7
		Mol. R.	+ ions	+ charges	Column 3 adjusted	+ ions adjusted for densities	
SiO_2	51.29	.8540	32.0	128.0	30.37	28.67	27.23
Al_2O_3	.64	.0063	.48	1.4	.46		
Fe_2O_3	2.00	.0125	.94	2.8	.89	5.12	4.85
FeO	33.66	.4684	17.55	35.1	16.66	11.38	10.80
MgO	6.36*	.1577	5.91	11.8	5.61	8.69	8.25
CaO	none						
Na_2O	.08	.0013	.10	.1	.09		
K_2O	.03	.0003					
$\text{H}_2\text{O}+$	5.54	.3074	23.04		21.90	} 26.34	25.02
$\text{H}_2\text{O}-$.24	.0133	1.00				
	99.84			179.2			
Mol. W.			3740		3551	3535	3358
Observed Density					3.01		2.86
Theoretical Density			3.18		3.02	3.01	

* It has been possible to determine MnO and TiO_2 . The table should read Al_2O_3 .61, TiO_2 .04, MgO 6.26, MnO .12; total 99.87.

MgO. Due to the present emergency it could not be determined at this time.*

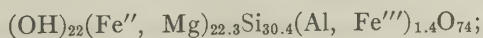
Column 2 of Table 3 contains the molecular ratios of the oxides; column 3 the number of cations in the structure based on the assumption that 32 Si ions are present as in two unit cells of talc. Column 4 tabulates the + charges of these cations. The charges due to H are omitted because as will be seen below, H is present as OH, in which capacity it occupies anion positions in the structure. The results of dehydration experiments on the mineral show that less than 3% of the H_2O+ can be driven off around 250°C. within three days. Above this temperature the FeO of the sample begins to oxidize. It is, therefore, concluded that practically all H_2O+ is present as OH. The molecular weight of the contents of column 3 is 3740. If this is put in the cell of the dimensions given above the density would be 3.18. This figure is much higher than the one observed when centrifuging the powder in Thoulet solution, where the settling of particles extended over a range from 3.03 to 2.99. Jolliffe (5, p. 415) reported a density of only 2.86, which is probably too low, particularly for material of his analysis. Ordinary talc has a theoretical density of 2.82. Also, as shown in the next paragraph and in column 7, Table 3, for a density of 2.86 the structure would not be balanced electrostatically, unless two O ions were omitted. Such a balance can be reached, however, if a density between that of column 6 and column 7 is assumed.

Two unit cells of talc contain $(OH)_{16}Mg_{24}Si_{32}O_{80}$ ions. There are 176 negative charges in 96 positions. These positions are probably always completely occupied since they form the "framework" between which the cations fill the small interstices. We have in minnesotaite 22 (OH) instead of 16 (OH). That leaves room for only 74 O. The total negative charges are $74 \times 2 + 22 = 170$. In column 4 we have 179.2+ charges. The number

of ions in column 3 must be multiplied, therefore, by a factor of $\frac{170.0}{179.2}$.

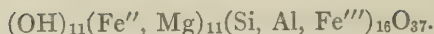
Column 5 is the result. The molecular weight of this column is 3551, which gives a theoretical density for minnesotaite of 3.02. This is in almost perfect agreement with the observed value.

We may safely assume that all of the Al and most of the Fe''' substitutes for Si, which is slightly deficient in amount. The formula then becomes:

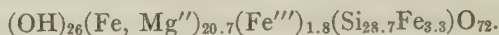


or, reduced to one unit cell and slightly simplified:

* See footnote under Table 3.

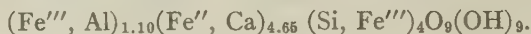


There is every reason to believe that minnesotaite varies in composition between considerable limits, particularly with regard to the ratio of Fe'' to Fe''' . For example, assuming a density of 3.01, the formula for Jolliffe's material (Table 3, column 6) would be:



This formula contains, however, 98 O and (OH) anions instead of the permissible 96. This suggests that not all H_2O of his analysis is present as (OH).

The idea of the replacement of O by (OH) is, of course, not new. It has been reported in the structure of phosphates, and Hendricks (10, p. 531) refers to such an arrangement in the layer silicate cronstedtite from Kisbanya, whose formula is:

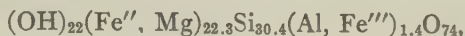


The formula in the original paper is incorrect. It contains too much (OH) and not enough O. Even in the corrected formula O_9 and $(\text{OH})_9$, instead of O_{10} and $(\text{OH})_8$, occupy the 18 available anion positions.

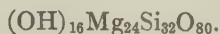
CONCLUSIONS

The identity of a mineral observed in thin sections for many years has been established as one with a talc structure but with about three-fourths of its Mg replaced by Fe. Talc analyses record a maximum of about 5% of Fe oxides. The name minnesotaite has been chosen for this mineral because it occurs in abundance in two of the three Minnesota iron ranges, the Mesabi and Cuyuna. In the Biwabik iron formation of the Mesabi range it is the most abundant of the three silicates with stilpnomelane and greenalite following in the order named. Richarz (4) and Jolliffe (5) have determined the optical properties of the mineral which apply to the nearly colorless variety as seen in thin sections. $N_\gamma - N_\alpha = 1.615 - 1.580 = 0.035$, parallel extinction, positive elongation, small optic angle with acute bisectrix normal to the perfect basal cleavage. Pleochroism may become distinct in the yellowish-green varieties, Z and Y = pale green and Z = pale yellow. It can be proved by x-rays that much darker colored varieties exist which are probably considerably higher in indices and stronger in pleochroism though they are so fine grained that only the properties of aggregates can be observed under the microscope. Minnesotaite has been found only in microscopic needles and plates. Its hardness is less than 3, its density for chemically analyzed material = 3.01, though Jolliffe has reported a value of 2.86 which the

author considers somewhat too low. The structure of the mineral was deduced from x -ray powder photographs and the size of its unit cell determined. Based on this, the density, and the chemical analyses, the formula for a unit cell is:



as compared with that of theoretically pure talc:



It is evident from these formulas that all 96 O and (OH) positions are filled but that minnesotaite has more (OH) and correspondingly less O, in order to balance the fewer + charges. As a matter of fact, if one is certain of the (OH) in the analysis he can calculate the chemical formula of the mineral without a knowledge of its density. This was done and an almost perfect agreement was obtained with the observed density.

Minnesotaite is associated with quartz (chert), siderite, magnetite, stilpnomelane, and greenalite. Many of the green granules which look exactly like greenalite in ordinary light, but are mottled, felt-like aggregates of greenish tints between crossed nicols, have been identified as minnesotaite by x -rays. Stilpnomelane, which had not been reported before from the Biwabik formation, occurs as very fine-grained needles and aggregates whose strong pleochroism is difficult to observe.

It is instructive to compare the three iron silicates with one another as to their structures and formulas:

Greenalite	(OH) ₁₂	(Fe'', Mg) ₉ Fe''' ₃	Si ₈	O ₂₂	· 2 H ₂ O
Stilpnomelane					
(K, Na, Ca) ₀₋₁	(OH) ₄	(Fe'', Mg, Al, Fe''') ₇₋₈	Si ₈	O ₂₃₋₂₄	· 2-4H ₂ O
Minnesotaite	(OH) _{8.5}	(Fe'', Mg) _{8.5}	(Si, Al, Fe''') ₈	O _{18.5}	

There is a decrease in total H₂O from greenalite to minnesotaite but an increase of SiO₂. All three contain MgO in appreciable quantities, but only stilpnomelane contains noteworthy amounts of Al₂O₃. The ratio of Fe'' to Fe''' varies considerably in all three. Greenalite has a serpentine structure (6). Stilpnomelane has a unique structure (8) which approximates that of mica or chlorite without, however, being a mixture of the two; while the structure of minnesotaite is similar to talc.

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SIDEROPHYLLITE FROM BROOKS MOUNTAIN, ALASKA*

ROBERT R. COATS AND JOSEPH J. FAHEY

ABSTRACT

A brittle, dark green mica (siderophyllite) from Brooks Mountain, Alaska, unusually high in divalent iron (30.16% FeO) and with almost no magnesia is described. The indices of refraction are: $\alpha=1.590$, $\beta=1.640$ and $\gamma=1.640$.

A specimen of mica from a granite pegmatite on Brooks Mountain, Seward Peninsula, Alaska, proved upon analysis to be siderophyllite, the rare high-ferrous member of the biotite group.

The name siderophyllite was given by Lewis,¹ in allusion to the large percentage of iron which it contains, "to a hard black mica" with "laminae very brittle" found in the neighborhood of Pike's Peak, Colorado.

As the feature that distinguishes his mica from previously described micas of high iron content is its large percentage of ferrous oxide (25.50%) and minor percentages only of ferric oxide (1.55%) and magnesia (1.14%), it can be inferred that Lewis intended to restrict the application of the name siderophyllite to micas having a similar composition. This restriction is here made explicit. The mica from Alaska described in this paper is therefore siderophyllite.

LOCATION AND MODE OF OCCURRENCE

Brooks Mountain is in the central part of the York Mountains, in the northwestern part of the Seward Peninsula, Alaska. The siderophyllite occurs in a pegmatite sill which is associated with a stock of coarse-grained porphyritic alaskite about 2 miles in diameter, forming the southern part of Brooks Mountain. The pegmatite sill, intrusive into fine grained marble, is exposed in one of two small pits about 500 feet northwest of a small ruined cabin on the saddle between the headwaters of Mint River and those of Crystal Creek, a tributary of Lost River. The sill consists of glassy gray quartz one foot thick, cut by stringers of siderophyllite and greenish-yellow orthoclase, both without crystal form. On the upper margin of the sill are masses of siderophyllite up to two inches in thickness, individual plates of which are as much as three-fourths of an inch across. The masses of coarse siderophyllite are locally separated from the altered limestone by massive orthoclase. On the

* Published by permission of the Director, U. S. Geological Survey, Department of the Interior, Washington, D. C.

¹ Lewis, H. C., On siderophyllite—a new mineral: *Proc. Acad. Natural Sci., Philadelphia*, 32, 254–255 (1880).

lower contact of the sill, the siderophyllite, orthoclase, and quartz are closely intergrown in a medium-grained allotriomorphic-granular aggregate.

In thin section the siderophyllite is pleochroic from dark green to pale straw yellow with a greenish tinge. Some plates of siderophyllite from the intergrowth on the lower contact are discontinuously rimmed by a thin shell of mica, pale blue in thin section, and with a double refraction of 0.028 and a $2V$ of 37° . No blue mica was observed, however, in the portion taken for analysis, which came from the coarse-grained siderophyllite in the upper margin of the sill. The orthoclase has been partly replaced by albite (Ab_{97}) in irregular perthitic veinlets and in small euhedral crystals along grain boundaries. The rock contains a few scattered grains of zircon and apatite.

The marble along the contact with the sill has been metasomatically altered for a thickness of three to five inches to a dark-green rock, cut by pinkish-brown irregular veinlets. Under the microscope the green rock is seen to consist principally of idocrase prisms about 2 mm. in diameter and scattered grains of green hornblende and magnetite. The idocrase encloses poikiloblastically very small anhedral grains of pleochroic hedenbergite ($Di_{30}He_{70}$) and euhedral colorless fluorite, and is replaced by hornblende, brownish green mica, and calcite. The veinlets are composed principally of garnet, with scattered grains of green hornblende and magnetite. The anhedral garnet grains, about 1 cm. in diameter, enclose poikiloblastically a little green hornblende and euhedral colorless fluorite, about 0.1 mm. in diameter. The sequence of formation appears to be hedenbergite, fluorite and idocrase; garnet, hornblende and magnetite; and calcite.

OPTICAL AND PHYSICAL PROPERTIES

The masses of siderophyllite correspond closely in color to Ridgway 35''''*m*, blackish green-gray. The cleavage flakes are brittle, unlike most mica—a fact commented on in the original description of siderophyllite.

The optical properties of the siderophyllite were determined on a part of the sample prepared for analysis. The greatest and least indices of refraction were measured in sodium light by oil immersion at room temperature. The optic angle was determined by Mallard's method, and β estimated from this value and the values for the other two indices.

$$\alpha = 1.590 \pm 0.002$$

$$\beta = 1.640 \text{ (calc.)}$$

$$\gamma = 1.640 - 1.642 \pm 0.002$$

$$B = 0.050$$

$$2V = 6-8^\circ$$

The birefringence was checked in thin section by means of a Berek compensator. The specific gravity is 3.121.

CHEMICAL ANALYSIS

The chemical analysis of the Alaskan siderophyllite is given in the following table under *A*. Under *B* is given the analysis of the original material described by Lewis,² and under *C* an analysis of siderophyllite from Ireland, described by Nockolds and Ritchey.³

ANALYSES OF SIDEROPHYLLITE

A. Siderophyllite from Brooks Mountain, Alaska; J. J. Fahey, *analyst*.

B. Siderophyllite from Pike's Peak, Colorado; H. C. Lewis and F. H. Genth, *analysts*.

C. Blue-green mica, Newcastle Co. Down, North Ireland, N. Sahlbom, *analyst*.

	A	B	C
SiO ₂	37.01	36.68	39.60
Al ₂ O ₃	15.89	20.41	22.80
Fe ₂ O ₃	Trace	1.55	.79
FeO.....	30.16	25.50	20.98
MgO.....	.22	1.14	.46
CaO.....	.10	.81	1.52
Li ₂ O.....	1.01	.37	None
Na ₂ O.....	.58	1.09	Trace
K ₂ O.....	9.02	9.20	8.95
Rb ₂ O.....	.19	—	—
Cs ₂ O.....	.12	—	—
H ₂ O—110°C.....	None	—	.24
H ₂ O+110°C.....	1.92	1.01	2.93
TiO ₂02	—	.21
MnO.....	1.01	2.10	.29
BaO.....	—	—	None
SrO.....	—	—	None
F.....	3.88	—	2.03
Cl.....	.24	—	—
	<hr/> 101.37	<hr/> 99.86	<hr/> 100.80
Less O.....	1.68		.85
	<hr/> 99.69	<hr/>	<hr/> 99.95
Sp. gr.....	3.121	3.1	3.04
α.....	1.590	—	1.582
β.....	1.640	—	1.625
γ.....	1.640	—	1.625

² Lewis, H. C., On siderophyllite—a new mineral: *Proc. Acad. Natural Sci., Philadelphia*, **32**, 254–255 (1880).

³ Nockolds, S. R., and Ritchey, J. E., Replacement veins in the Mourne Mountains granite, North Ireland: *Am. Jour. Sci.*, **237**, 27–47 (1939).

A sample was prepared for analysis by grinding the material in an agate mortar, sieving through a 60-mesh screen and discarding that portion passing a 100-mesh screen. A minor quantity of quartz was then removed by heavy-liquid separation (bromoform having a specific gravity 2.836). The sample was then washed well with acetone and dried at room temperature. The five alkalis were determined by the procedure published by Wells and Stevens,⁴ silica and fluorine by the ferron colorimetric method,⁵ and the remaining constituents by the methods recommended by Hillebrand and Lundell.⁶

From the analyses in the table it is seen that the percentage of ferrous oxide is higher (30.16%) and those of ferric oxide and magnesia lower (trace and 0.22%, respectively) in the Brooks Mountain mineral than in the sample described by Lewis. Other features of analysis *A* are the low CaO, the high Li₂O and F, and the chlorine content.

The high-iron biotite (26.72% FeO and 2.87% Fe₂O₃) from Amelia, Virginia,⁷ in which MgO was not determined may closely approach siderophyllite. The rastolyte of Shepard⁸ with 38.25% total iron computed to FeO cannot be listed as siderophyllite because trivalent iron was not determined. The same is true of several other analyses of micas containing from 32 to 28 per cent of total iron expressed as FeO. The literature also presents other analyses of biotite containing more than 25% FeO, but these have 4 to 9 per cent Fe₂O₃ and therefore should be classed as lepidomelane. The Brooks Mountain biotite described in this paper is the third known occurrence of siderophyllite.

STRUCTURAL CLASSIFICATION AND FORMULA

As the mineral is a mica there was little question that the atomic structure was one having the silicon atoms arranged in continuous sheets, but its peculiar composition made it interesting to derive the exact formula according to the modern method of *x*-ray classification. As a matter of fact the analysis shows that it has very nearly the composition of a pure end member.

The accompanying table shows the number of metallic atoms calculated for 10 atoms of oxygen.

⁴ Wells, R. C., and Stevens, R. E., Determination of the common and rare alkalis in mineral analysis: *Ind. Eng. Chem., Anal. Ed.* **6**, 439-442 (1934).

⁵ Fahey, J. J., Colorimetric determination of fluorine with ferron: *Ind. Eng. Chem., Anal. Ed.*, **11**, 362-363 (1939).

⁶ Hillebrand, W. F., and Lundell, G. E. F., *Applied Inorganic Analysis*. John Wiley and Sons, Inc., New York (1929).

⁷ Glass, Jewell J., The pegmatite minerals from near Amelia, Virginia: *Am. Mineral.*, **20**, 748 (1935).

⁸ Dana, J. D., Fourth supplement to Dana's Mineralogy: *Am. Jour. Sci.*, **24**, 128 (1857).

	<i>A</i>	<i>B</i>	<i>C</i>
Si.....	2.976	2.599	2.966
Al.....	$\left\{ \begin{array}{l} 1.024 \\ .482 \end{array} \right\}$	$\left\{ \begin{array}{l} 1.401 \\ .303 \end{array} \right\}$	$\left\{ \begin{array}{l} 1.034 \\ .978 \end{array} \right\}$
Fe ^{III}	—	.083	.044
Fe ^{II}	2.028	1.510	1.313
Ti.....	—	—	.012
Mn.....	.069	.126	.018
Li.....	.327	.106	—
Mg.....	.027	.120	.051
Ca.....	.009	.061	.122
Na.....	.091	.150	—
K.....	.925	.831	.855
Rb.....	.010	—	—
Cs.....	.004	—	—
OH.....	1.029	.477	1.463
F.....	.986	—	.480
Cl.....	.033	—	—
	$\left. \begin{array}{l} 4.00=Z \\ 2.93=Y \\ 1.04=X \\ 2.05 \end{array} \right\}$	$\left. \begin{array}{l} 4.00=Z \\ 2.25=Y \\ 1.04=X \\ 0.48 \end{array} \right\}$	$\left. \begin{array}{l} 4.00=Z \\ 2.42=Y \\ 0.98=X \\ 1.94 \end{array} \right\}$

As seen in the table the Brooks Mountain siderophyllite (*A*) approaches very closely to the theoretical octaphyllite molecule $\text{XY}_3\text{Z}_4\text{O}_{10}(\text{OH}, \text{F})_2$ of the phlogopite and biotite micas, in which the value of *Y* is three. *X* is close to 1. *Y*₃ is very largely ferrous iron and Mg is only 0.027, which are the characteristic features for designating the mica as siderophyllite. The ratio of Si to Al in the Z group is very close to 3:1. If analysis *B* is correct, on the other hand, the Pike's Peak siderophyllite has less Al in the *Y* group than either of the other two.

The heptaphyllite molecule $\text{XY}_2\text{Z}_4\text{O}_{10}(\text{OH}, \text{F})_2$ of muscovite in which *Y* = 2, seems to predominate in the Pike's Peak mineral (*B*) in which *Y* = 2.25, and in the sample from the Mourne Mountains (*C*) in which *Y* = 2.42. The low figure (0.48) for the (OH, F) group in analysis *B* is due to the fact that fluorine was not determined and to the faulty method "moderate ignition" used for the determination of water.

That this analysis is incorrect, having a deficiency of anions, i.e. $\text{O}_{10}(\text{OH})_{0.48}$, can further be shown by recomputing to a total of twelve oxygen atoms. This makes the value of *X* more than one (1.194) and the value of *Y* more than three (3.153), a condition that does not fit the structure of mica.

In addition to the type analysis (*B*) there has been published only the one complete analysis (*C*) of material that can be classified as siderophyllite. The Brooks Mountain siderophyllite (*A*) is nearer than the type material to what could be called the ultimate composition of siderophyllite, in which all of the aluminum in the octahedral position in muscovite is replaced by divalent iron, yielding the formula $\text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$. Such a mineral would contain 42.12% FeO.

CLAY MINERALS IN LAKE ERIE SEDIMENTS

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ABSTRACT

A clay-mineral and petrographic study has been made of 14 different samples of sediments from the bottom of Lake Erie. Thermal analyses, optical studies, and *x*-ray diffraction patterns have been used to determine the nature of the clay-mineral composition of these sediments. The data indicate that the predominant clay-mineral is of an illite character.

The analyses of these samples show a good correlation between the depth of water under which the samples were secured, their location with regard to shore line, and the amount and character of residue (particles greater than two microns in diameter) and clay (particles smaller than two microns in diameter).

INTRODUCTION

Clay-mineral studies and petrographic studies of sediments have been made of numerous different types of materials in the last few years (1). The clay-mineral composition has been determined of shales, clays, soils, limestones, dolomites, and of ocean sediments utilizing techniques which have become popular for this type of work. They are thermal analysis, optical studies, *x*-ray analysis, and chemical analysis. It was thought advisable to apply some of the same techniques to fresh water lake sediments in order to determine their character.

The present paper deals with a study of samples obtained during a cooperative survey made of Lake Erie in 1928 and 1929 by the United States Bureau of Fisheries, the New York State Conservation Department, the Ontario Department of Game and Fisheries, the Health Department of the City of Buffalo, and the Buffalo Society of Natural Sciences (2, 3). Thermal analyses, optical studies, and *x*-ray analyses were made of these samples with the particular object of determining their clay-mineral composition.

The samples studied are as representative of the many variations offered that it was possible to obtain. Some are from locations in the deepest part of Lake Erie; some from comparative shallows; and some are from locations where the bottoms are known to be composed of sand, limestone, or mud.

The locations from which the various samples were collected are shown in Fig. 1. The sample numbers and the depth of the water at the location from which the samples were taken are given in Table 1 in order of increasing depth.

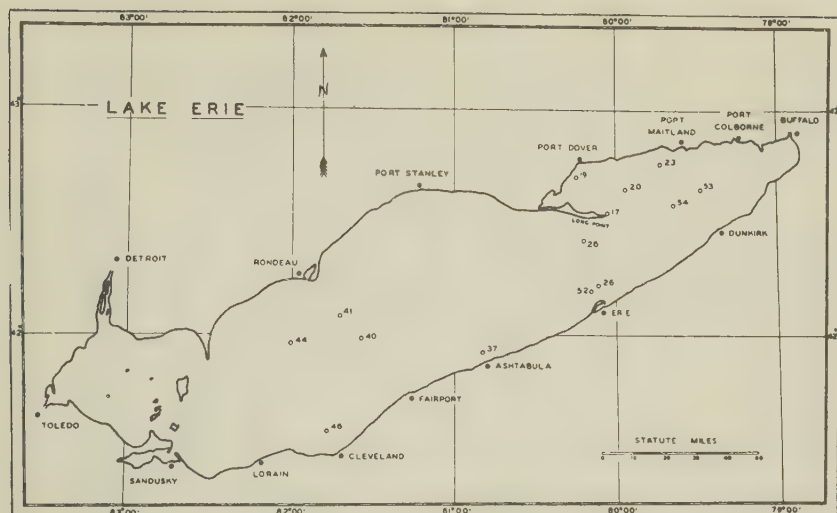


FIG. 1. Map of Lake Erie showing the number and location from which the samples were collected.

TABLE 1

Sample Number	Depth in Meters	Per Cent Loss of CO ₂ and O.M.*	Per Cent Clay	Per Cent Residue
19	9.0	22.4	9.0	68.6
52	13.5	22.8	10.1	67.1
37	17.0	9.2	25.4	65.4
46	18.0	11.0	35.2	53.8
26	21.0	9.1	11.5	79.4
23	21.0	17.9	15.8	66.3
44	23.0	9.3	52.0	38.7
17	24.0	16.5	4.3	79.2
41	24.0	6.7	44.1	49.2
40	24.0	5.5	64.5	30.0
53	29.0	12.2	19.5	68.3
28	35.0	16.9	32.2	50.9
20	37.0	11.5	39.6	48.9
54	52.0	11.7	35.9	52.4

* Organic matter.

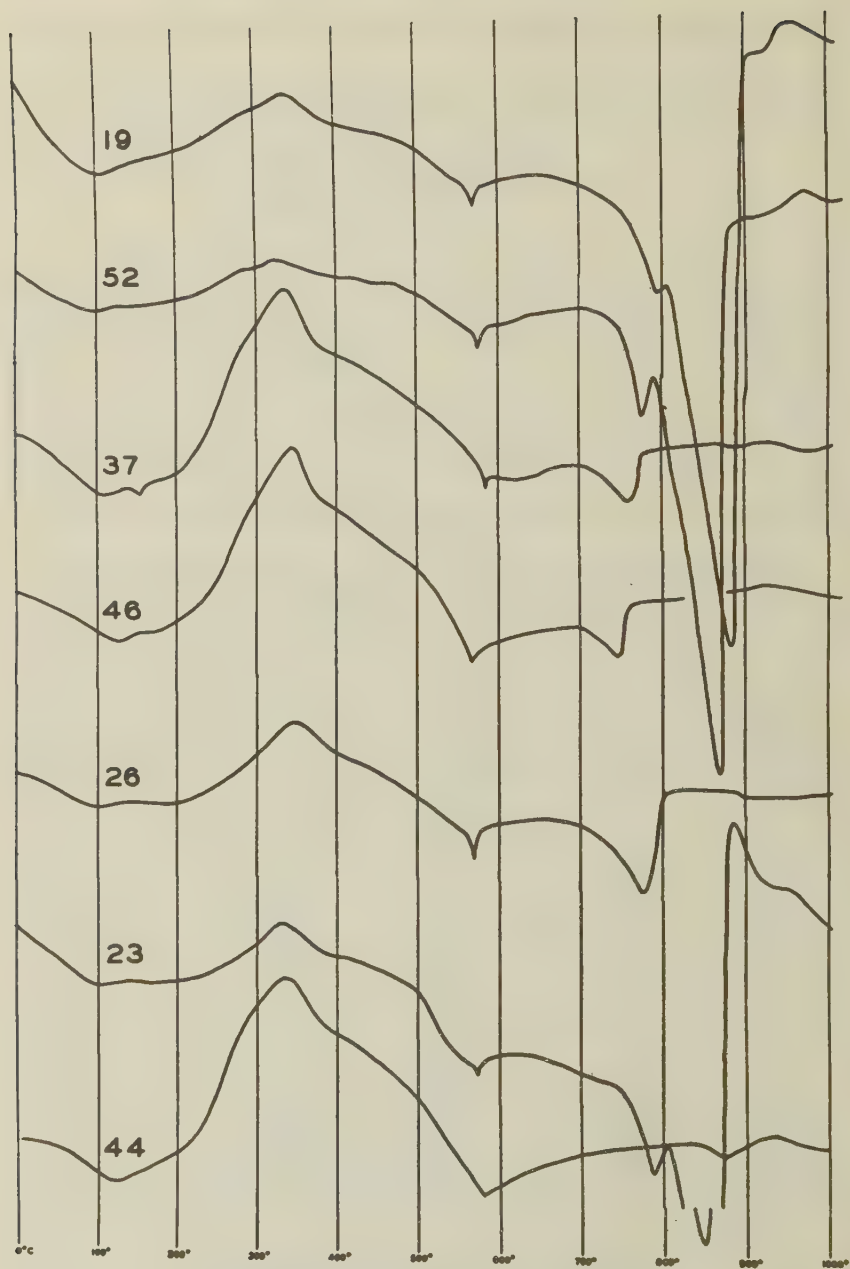


FIG. 2. Differential thermal analyses of untreated samples.

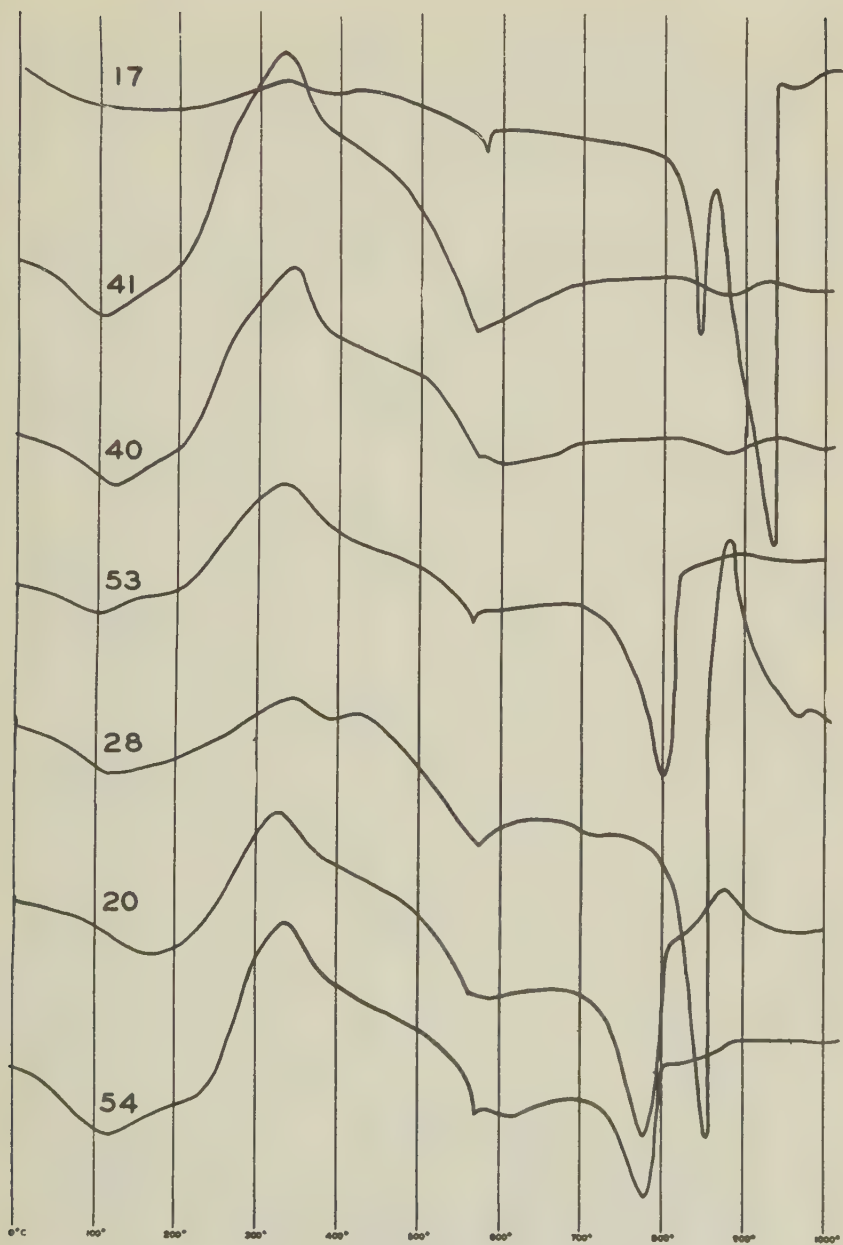


FIG. 2 (*continued*). Differential thermal analyses of untreated samples.

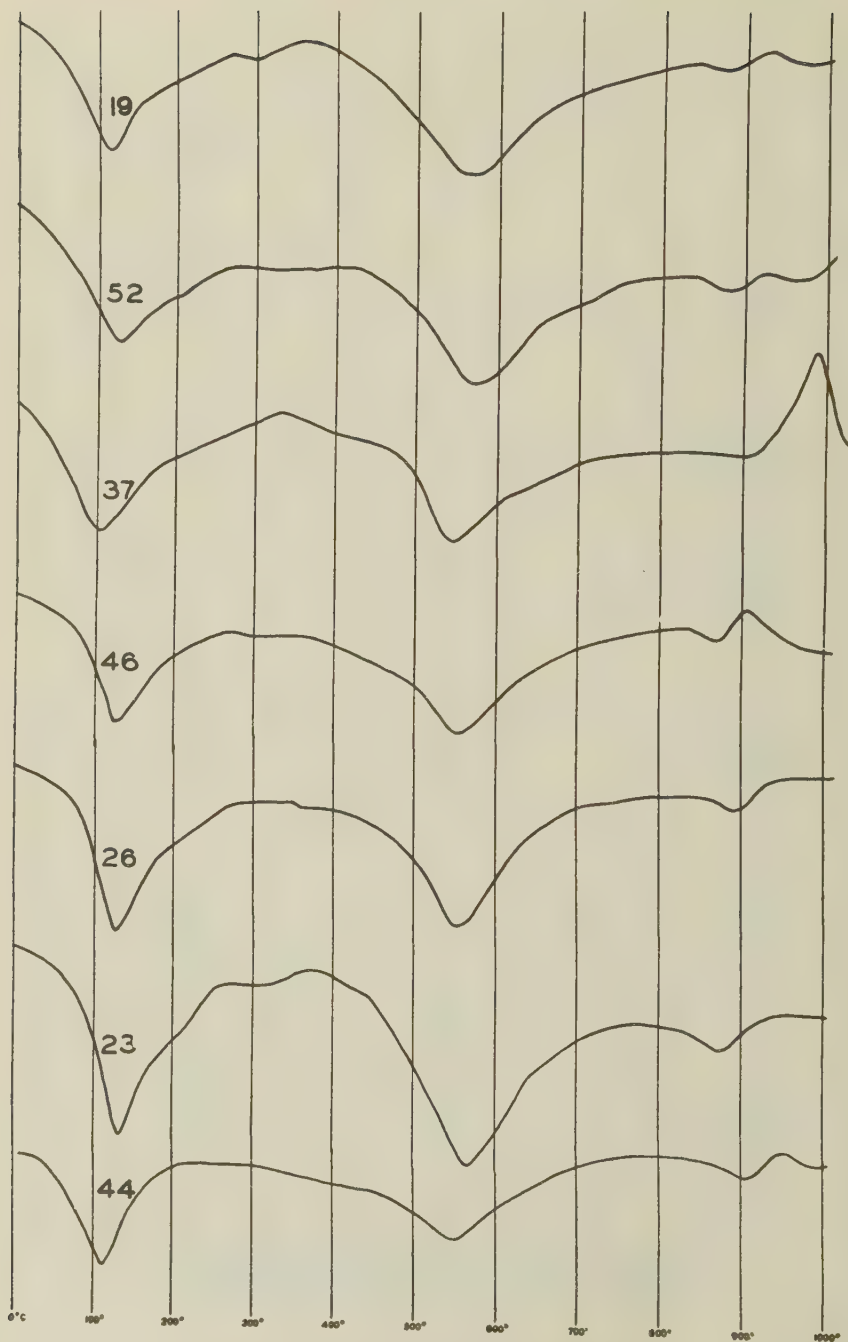


FIG. 3. Differential thermal analyses of clay fractions.

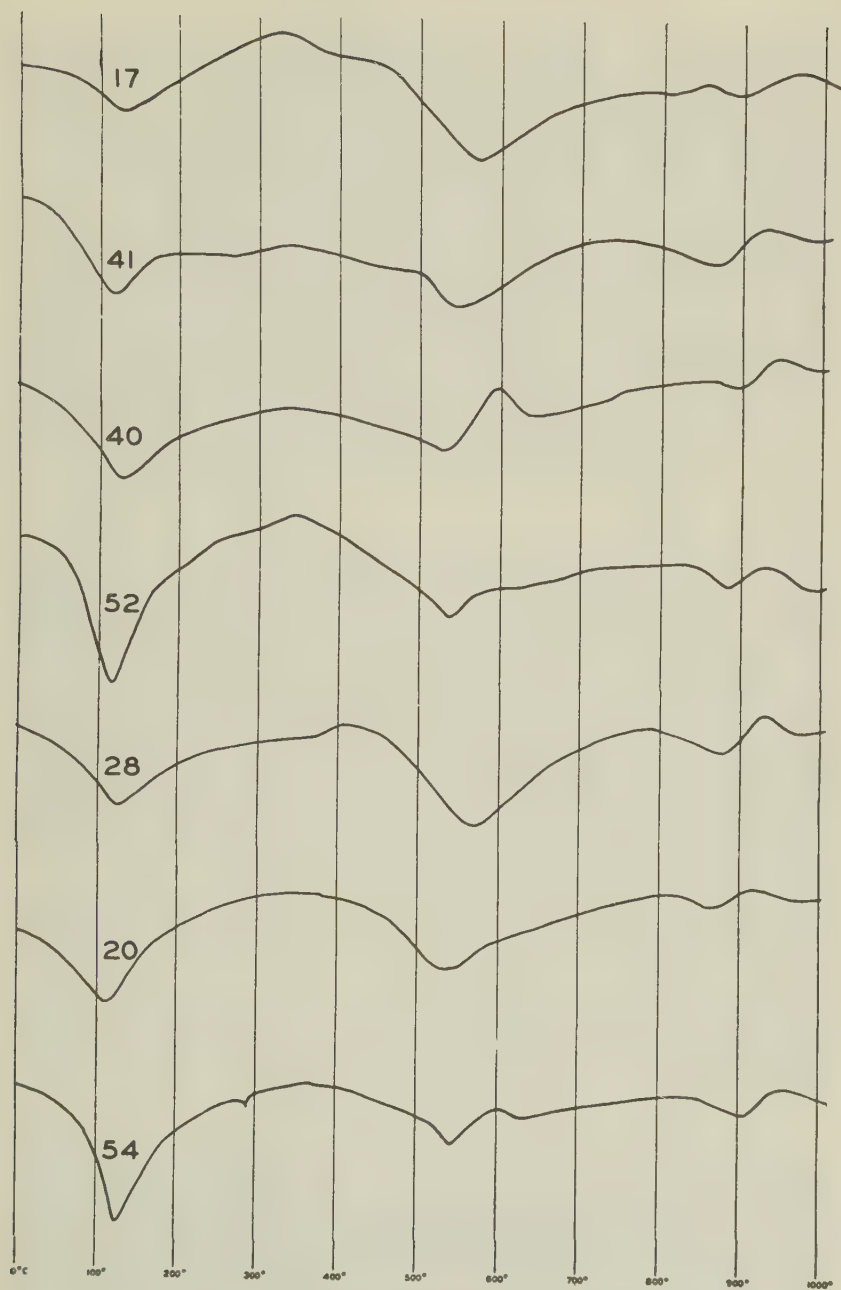


FIG. 3 (continued). Differential thermal analyses of clay fractions.

EXPERIMENTAL PROCEDURE

Differential thermal analyses were made of samples representative of the materials as collected in order to obtain information on the composition of the whole samples. The apparatus used is like that commonly used in this work and has been described before (4). Figure 2 shows the thermal diagrams of the whole samples in their original condition.

The samples were then treated with dilute hydrochloric acid and hydrogen peroxide in order to destroy the carbonates and organic matter. The organic matter was destroyed following the method of Bray (5). This was necessary to obtain a fractionation of the samples and to allow concentration of the clay-minerals for further and more complete identification. Also by destroying the carbonates and organic matter the thermal reactions of the remaining materials are less apt to be obscured by the more vigorous reactions of the carbonates and organic material. The percentages of carbonates and organic matter removed by this treatment are given in Table 1.

The treated samples were then put into suspension by the addition of ammonium hydroxide and a fractionation was made at two microns effective particle size by siphoning that part of the suspension containing only particles two microns or less in diameter. A fractionation of this type concentrates the clay-minerals in one fraction, the colloid, and the non-clay-minerals in another fraction, the residue. This facilitates identification of the clay-minerals by all types of analyses. The fractionation was repeated until the separation was considered complete. Table 1 shows the per cent of clay-mineral (consisting of particles smaller than two microns in diameter) and the per cent of residue (consisting of particles greater than two microns in diameter).

Differential thermal analyses were then made of each of the clay fractions of the samples. Diagrams representing these analyses are given in Fig. 3.

Both the residue and clay fractions of all the samples were studied microscopically and x-ray diffraction patterns were secured of several of the clay fractions.

EXPERIMENTAL RESULTS

Untreated samples

Differential thermal analyses of the untreated, whole samples practically all show slight endothermic reactions at about 125°C. This initial reaction is due to the primary dehydration of adsorbed water. For some of the samples, Nos. 37, 46, 44, 41, 40, 53, 20, 54, this reaction is followed by an exothermic reaction between 200°C. to 500°C., which is the burning

off of the organic matter. All of the curves have the typical quartz endothermic reaction at about 560°C. The sharpness and magnitude of this reaction is semi-quantitative and can be correlated to a degree with the fractionation data given in Table 1. The endothermic reaction between about 750°C. and 950°C. is believed to be caused by the presence of carbonates, probably both calcium and magnesium carbonates, and combinations of both, such as dolomite.* No indication of the amount and type of clay is indicated in any of these diagrams with the possible exception of Nos. 44, 41, and 40.

Microscopic study of the whole samples revealed the coarse, non-clay, inorganic part of all the samples contained quartz, sand, shell fragments, limestone, dolomite, and rock fragments. Many of the samples had to be carefully washed in distilled water in order to permit determinations of the constituents.

Treated clay fractions

By destroying the carbonates and organic matter as described in the procedure, and by separating the clay or minus two micron material, thermal analyses are made of value for determining the type of clay. Figure 3 shows the differential thermal analyses of the clay fraction of these samples. In contrast to the diagrams for the whole samples, the initial dehydration reaction is much sharper and entirely completed at about 125°C. which is common in clays. This reaction is followed by another endothermic reaction at about 550°C. and by double endothermic, exothermic reaction between 850°C. and 1000°C. These reactions are believed to be indicative of an illite type of clay-mineral.

The striking similarity of all the curves is noteworthy. For all samples the effectiveness of the removal of the carbonates, organic matter, and quartz is clearly shown.

Microscopic study revealed that the clay fractions (minus two microns, effective diameter) were too coarse to allow accurate determination of optical properties. Practically all of the material had a mean index refraction of about 1.56. Some of the samples were redispersed and a small amount of the very finest material collected. The optical properties of this material were: $\gamma = 1.582$ to 1.606 , $\gamma - \alpha = .032$ to $.036$ (-) and it appeared to be quite pure.

X-ray diffraction analyses were secured of four of the clay samples chosen to be representative of the entire group; Nos. 52, 26, 17, 28. With the exception of the diffraction lines of quartz, few well defined diffraction

* Unpublished work by R. A. Rowland and F. L. Cuthbert.

lines were obtained. The patterns strongly suggest that the bulk of the material represents a random growth of mixed layers with frequent indications of small amounts of material of a glauconitic and montmorillonitic type.

DISCUSSION AND SUMMARY

The application of modern techniques of clay analysis are shown to be of great aid in studying fresh water lake sediments. Differential thermal analyses are of value, particularly when coupled with optical and *x*-ray studies, not only in determining the nature of the clays but also to obtain an approximation of the general composition of the entire sample.

Relation of the composition of the samples to location

The analyses of the whole samples show a good correlation between depth of sample, location of sample with regard to shore line, amount of clay material. The samples, as collected, or in the raw state, are composed largely of quartz, carbonates, organic matter, and clay of varying percentages. Those samples, collected from shallow areas of the lake, Nos. 19, 52, 37, contain large amounts of non-clay material as shown by both thermal analyses and by the fractionation data. Also, samples from locations near the shore line, Nos. 17, 26, 23, are shown to contain little clay, more or less independent of the depth. Samples from the deeps or from areas near the middle of the lake contain the largest amounts of clay and smallest amounts of quartz and carbonates, Nos. 40, 44, 41, and 54. Sample No. 20, while from a comparatively deep part of the lake, 37 meters, is also quite close to shore. The location is in Long Point Bay which is known to have a muddy bottom. Consequently, the sample contains a relatively high per cent of clay.

Type of clay-mineral present

The clay fraction of the samples is believed to be composed largely of an illite-type of material that is commonly present in soil materials, shales, etc. This conclusion is supported by the thermal curves, characterized by the relatively small initial dehydration peak, the endothermic reaction at about 550°C. and the smaller, double endothermic, exothermic reaction between 850°C. and 1000°C. The optical data for the purer clay is within the range of values reported for other illite clays.

X-ray diffraction patterns, secured on four samples, indicate that much of the material is not well crystallized but rather follows a pattern of random growth, perhaps an intimate mixture of layers of different clay-

minerals. This intermingling of layers of different clay-minerals has been reported before and is thought to occur more or less commonly, particularly in complex systems like soils.

While the x -ray data do not appear, at first glance, to substantiate the conclusions derived from the differential thermal analyses and the optical studies, such discrepancies are not at all unusual when working with materials of this nature. Due to the poor degree of crystallization it is difficult to interpret the diffraction patterns obtained in terms of well-defined clay-minerals. The data indicate the necessity of using as many methods of analyses as possible when attempting to make clay-mineral determinations of materials of this nature.

Source of sediments

The source of these Lake Erie sediments, in view of this work, affords an interesting problem for speculation. The rocks of the Lake Erie basin are Devonian in age and composed almost entirely of shales; the Chemung, Portage, Genesee, Hamilton, and Marcellus formations. The Onondaga formation, a massive limestone, is the only formation of any significance that is not shaly, and outcrops almost entirely on the northern side of the lake. While no clay-mineral analyses are known to be available of these shales, it can be supposed that they would be illite in nature. Also, the glacial till, which practically covers the drainage area of Lake Erie, may well be the source of the clay sediments.

The presence of carbonates in the samples, aside from the shell fragments noted, can also be expected when we consider the large areas of exposed limestone and dolomitic rocks in the immediate vicinity of Lake Erie.

More detailed investigations of the clay-mineral nature of fresh water lake sediments should present interesting results leading to a better understanding of the genesis of clay-minerals. Similar studies should also aid in understanding the history of many of our commercial clay deposits as many are located in the basins of extinct lakes.

ACKNOWLEDGMENTS

Appreciation is expressed to the following: Dr. R. H. Pegrum, who provided the samples to make the work possible; The Illinois State Geological Survey in whose laboratories the analytical work was carried out; Dr. W. F. Bradley of the Illinois State Geological Survey who made the x -ray diffraction patterns; and Dr. R. E. Grim of the same organization, who offered many helpful suggestions during the writing of the manuscript.

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BUTYL "CARBITOL" AS AN IMMERSION LIQUID

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ABSTRACT

Butyl "carbitol" [2 (butoxyethoxy) ethanol] has the following properties which make it desirable as the low index end-member of a series of immersion liquids prepared by mixing it with 1-chloronaphthalene: (1) low dispersion, (2) low temperature coefficient, (3) very stable, (4) colorless and nearly odorless. Graphs are presented showing variation of dispersion with index of refraction, and variation of index of refraction with temperature, for butyl "carbitol"—1-chloronaphthalene liquids.

INTRODUCTION

The optical properties of ideal immersion liquids have been discussed by Buerger (1933), who points out that the most desirable constituents for a set of immersion liquids should have the following properties in common: (1) equal dispersion, (2) equal temperature coefficients. It is desirable also that they have equal vapor pressures at ordinary temperatures, and good keeping qualities.

It is impossible to attain the goal of an ideal series of liquids. However, the ideal may be most closely approached if a series of liquids is prepared by mixing two miscible end-members of as widely different index as possible, provided the end-members have the necessary properties mentioned above. If the set of liquids is made by mixing only two end-members, then even though they do not have equal temperature coefficients and dispersion, these two properties will vary continuously from one end of the set to the other.

Many substances have been proposed for preparing a set of immersion liquids to cover the refraction range between 1.45 and 1.66. Butyl "carbitol"¹ [2 (butoxyethoxy) ethanol; diethylene glycol mono-butyl ether] has several properties that make it highly desirable as the low index end-member of a series of liquids in the intermediate range. A set of liquids prepared by using butyl "carbitol" and 1-chloronaphthalene (α -monochloronaphthalene) as end-members has been in use for the past three years in the Yale Mineralogical Laboratory. It has proved to be more satisfactory than any previously used.

DESCRIPTION OF PROPERTIES

Butyl "carbitol" and 1-chloronaphthalene are miscible in all proportions and when used as end-members provide a continuous series from 1.43 to 1.63. 1-bromonaphthalene would serve equally well as the higher

¹ Manufactured by the Carbide and Carbon Chemicals Corporation, 30 East 42nd Street, New York, N. Y.

end-member of the series, and its use would extend the set of liquids to 1.66.

The properties of a set of immersion liquids prepared with butyl "carbitol" and 1-chloronaphthalene are described below.

Dispersion. The dispersion of the two end-members and several intermediate members of the set was measured with an Abbé refractometer. A graph of these values (Fig. 1) shows that there is a straight line relation between dispersion and index of refraction. From Fig. 1 the dispersion of any intermediate member of the set of immersion liquids may be found.

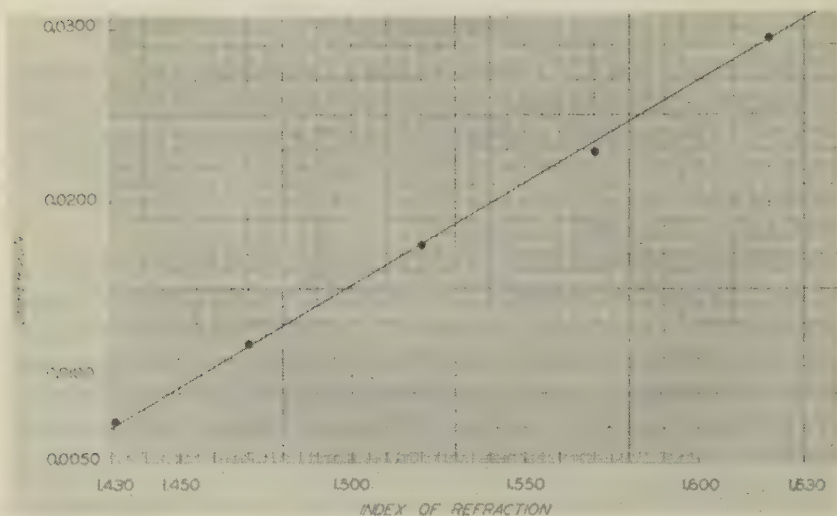


FIG. 1. Dispersion ($n_F - n_C$), plotted against index, n_D , for butyl "carbitol"—1-chloronaphthalene liquids.

Temperature coefficient. The temperature coefficient, dn/dt , was determined for the two end-members and four intermediate members of the set of index liquids. In Fig. 2 the temperature coefficient is plotted against index of refraction. From this graph dn/dt may be determined for any liquid of the set.

Stability. Butyl "carbitol" and 1-chloronaphthalene have boiling points of 231.2°C. and 281.1°C., respectively. Thus at room temperatures they must both have relatively low vapor-pressures. To test their differential rate of evaporation five cc. of several liquids of the set were placed in 75 mm. watch glasses and allowed to stand for 70 hours at room temperature. The maximum change in index of refraction was 0.003. Thus for the ordinary period of time during which immersion liquids are used on a microscope slide (during which time they are covered with a cover slip) the change in index due to differential evaporation would be negligible.

The set of butyl "carbitol"—1-chloronaphthalene immersion liquids being used by the writer has been in constant use for three years. At the time this set of liquids was prepared they were calibrated to ± 0.001 . Re-calibration at the end of three years has revealed a maximum change in index of 0.001, and in most cases less than this. The liquids have been stored in standard double-stoppered bottles.

Other properties. Butyl "carbitol" is a colorless, almost odorless, slightly viscous liquid. Immersion liquids prepared by mixing butyl "carbitol" and 1-chloronaphthalene are colorless and remain that way indefinitely.

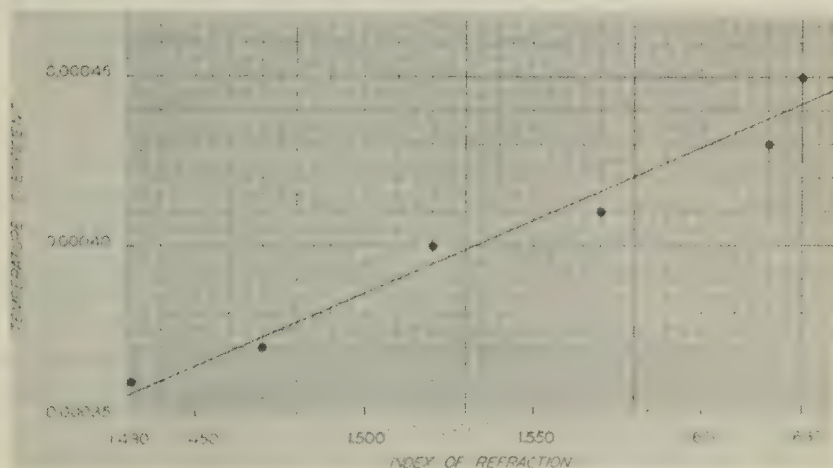


FIG. 2. Temperature coefficient, dn/dt , plotted against index, n_D , for butyl "carbitol"—1-chloronaphthalene liquids.

Butyl "carbitol" is miscible in all proportions with water. Hence by using water and butyl "carbitol" as end-members a series of liquids may be readily prepared to cover the range between 1.34 and 1.43. Liquids prepared in this way are quite stable, and very satisfactory in most respects. Unfortunately their use is limited by the fact that most minerals in this range are water-soluble.

ACKNOWLEDGMENTS

The writer learned of the possibilities of butyl "carbitol" as an immersion liquid through Dr. Harry Berman of Harvard University. Its use was suggested to Dr. Berman by Dr. C. D. West, of the Polaroid Corporation, Cambridge, Mass. Grateful acknowledgment is due Dr. West and Dr. Berman for permission to prepare this paper.

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NOTES AND NEWS

BOUSSINGAULTITE FROM RESIDUE OF FIRE IN ANTHRACITE REFUSE BANK¹

(Contribution from the Central Experiment Station,
Bureau of Mines, Pittsburgh, Pa.)

WILDER D. FOSTER²

INTRODUCTION

This paper contains a description of the occurrence of boussingaultite, $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, following a fire³ in a bank of minus-eight-inch anthracite breaker refuse two miles west of Mahanoy City, Schuylkill County, Pennsylvania, in the Western Middle anthracite field.

A series of 17 holes was drilled into the refuse to locate the fire. The hole (No. 3) around which the boussingaultite was discovered was drilled until hot vapors were encountered at a depth of 158 feet. The temperature at the bottom of this hole was 370°C., while that in the other holes did not exceed 100°C. About 30,000 pounds of limestone dust in a 1 to 1 aqueous suspension was poured down this hole No. 3 to aid in extinguishing the fire. The dust was found, upon excavation of the burning refuse, to have spread 6 to 8 feet radially from the holes not in the hottest zone and to have traveled to the outer limits of the fire and deposited as a chalk-like mass from the holes in the hottest zone.

DISCOVERY OF THE BOUSSINGAULTITE

Pinkish crystals of boussingaultite were found, upon excavation of the burned refuse, filling cavities in the refuse near the edges of the deposits of the limestone dust. Refuse material (consisting of unburned, high-grade anthracite, bone coal, and slate) was found cemented together by some of the crystals. The presence of the unburned coal, which has an ignition temperature of 470°C.,⁴ indicates that the sample was not heated higher than this temperature, even though the refuse reportedly⁵ burned to ashes. The boussingaultite evidently formed after the hot refuse cooled

¹ Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior, Washington, D. C.

² Assistant chemist-petrographer, Gas and Dust Section, Central Experiment Station, Bureau of Mines, Pittsburgh, Pa.

³ Leitch, R. D., Some information on extinguishing an anthracite refuse-bank fire near Mahanoy City, Pa.: *Bureau of Mines, Inf. Circ.* 7104, 16 pp. (1940).

⁴ Jones, G. W., and Scott, G. S., Chemical considerations relating to fires in anthracite refuse: *Bureau of Mines, Rept. of Investigations* 3468, 5 (1939).

⁵ Leitch, R. D., Work cited in footnote 3, page 15.

as ammonium-magnesium sulfate hexahydrate loses 86 to 87 per cent of its water at 120°C. and becomes anhydrous at 132°C., according to Mellor.⁶ Boussingaultite crystallizes, without decomposition, from an aqueous solution.⁷ Thus the formation of boussingaultite from components in solution would be expected upon evaporation or cooling of the solution.

IDENTIFICATION OF THE BOUSSINGAULTITE

The crystals varied in color from colorless to a yellowish-pink and were about 1 mm. in diameter. Some had small faces. Most of the crystal fragments revealed, under the microscope, a centered optic normal interference figure due to the {010} cleavage. The material was biaxial positive with $\alpha = 1.471 \pm 0.002$ and $\gamma = 1.479 \pm 0.002$, and had a moderate $2V$ and a birefringence of 0.008. An extinction angle was not measured.

The material was soluble in water and yielded water upon heating in a closed tube. Ammonia⁸ and sulfate⁹ were found by chemical microscopy.

Considerable magnesium, a few tenths of one per cent of iron and manganese, and traces of calcium and silicon were found by spectroscopic analysis.¹⁰ The iron and manganese probably replaced some of the magnesium.

PROBABLE ORIGIN OF THE BOUSSINGAULTITE

Ammonical compounds in the refuse probably supplied the ammonia for the boussingaultite. Leitch¹¹ noted a faint odor of ammonia during the pouring of the limestone suspension. Liberation of ammonia was attributed to the action of free lime from the limestone on ammonical compounds in the refuse. The formation of an ammonium-calcium sulfate might be expected in the presence of the quantity of calcium carbonate present in the drill hole. An ammonium syngenite has been reported¹² but it is stable only in strong ammonium sulfate solutions.

Magnesium in the limestone, in ankerite in the coal, and in the water of the limestone suspension probably supplied the magnesium. The lime-

⁶ Mellor, J. W., *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*: Longmans, Green & Co., London, 4, 342-343 (1923).

⁷ Weston, A., The quaternary system potassium sulfate—magnesium sulfate—ammonium sulfate—water: *Jour. Chem. Soc.*, 121, 1223-1237 (1922).

⁸ Add sodium hydroxide to solution and warm. Odor of ammonia was obtained upon heating the solution to which sodium hydroxide was added.

⁹ Gypsum crystals were formed upon addition of calcium acetate to the solution.

¹⁰ Analysis by H. I. Oshry, former assistant physicist, Gas and Dust Section, Central Experiment Station, Bureau of Mines, Pittsburgh, Pa.

¹¹ Leitch, R. D., Work cited in footnote 3, page 3.

¹² Hill, A. E., and Yanick, N. S., Ternary systems. XX. Calcium sulfate, ammonium sulfate, and water: *Jour. Am. Chem. Soc.*, 57, 645-651 (1935).

stone, judging from analysis¹³ of samples from the vicinity of its origin¹⁴ (Bellefonte, Centre County, Pennsylvania), probably contained about 0.5 per cent MgCO_3 . Thirty thousand pounds of limestone with 0.5 per cent MgCO_3 would contain 150 pounds of MgCO_3 , which is equivalent to 640 pounds of boussingaultite. Some of the bone coal from the vicinity of the boussingaultite was found to contain a few per cent of ankerite. The water, judging from analysis of water from a nearby well¹⁵ and from the Susquehanna River¹⁶ (into which the region drains), contained only a few parts per million of magnesium, so the water was not an important source of the magnesium. Lansfordite and nesquehonite, the type locality of which is about 20 miles away,¹⁷ may have contributed some magnesium but none of these minerals were found in the samples of boussingaultite.

Sulfur compounds in the refuse probably supplied the sulfur for the sulfate. From 0.2 to 4.3 per cent sulfur was found¹⁸ in similar refuse.

¹³ Miller, B. L., Limestones of Pennsylvania: *Pa. Geol. Sur.*, 4th Series, *Bull.* **M20**, 281-291 (1934).

¹⁴ Personal communication, George E. McElroy, senior mining engineer, Health Division, Central Experiment Station, Bureau of Mines, Pittsburgh, Pa.

¹⁵ Lohman, S. W., Ground water in northeastern Pennsylvania: *Pa. Geol. Sur.*, 4th Series, *Bull.* **W4**, 244 (1937).

¹⁶ Dole, R. B., The quality of surface waters in the United States: *U. S. Geol. Sur.*, *Water-Supply Paper* **236**, 104 (1909).

¹⁷ Ford, W. E., *Dana's Textbook of Mineralogy*: John Wiley & Sons, New York (1932), pp. 529-531.

¹⁸ Jones, G. W., and Scott, G. S., Work cited in footnote 4, page 5.

NOMINATIONS FOR OFFICERS OF THE MINERALOGICAL SOCIETY OF AMERICA FOR 1945

The Council has nominated the following for officers of the Mineralogical Society of America for the year 1945:

PRESIDENT: K. K. Landes, University of Michigan, Ann Arbor, Michigan.

VICE-PRESIDENT: George Tunell, Geophysical Laboratory, Washington, D. C.

SECRETARY: C. S. Hurlbut, Jr., Harvard University, Cambridge, Mass.

TREASURER: Earl Ingerson, Geophysical Laboratory, Washington, D. C.

EDITOR: Walter F. Hunt, University of Michigan, Ann Arbor, Michigan.

COUNCILOR (1945-1948): R. E. Grim, Illinois Geological Survey, Urbana, Illinois.

Following the decision of the Geological Society of America, there will be no meeting for the presentation of papers of the Mineralogical Society of America during 1944. Members of the Society may submit abstracts of scientific papers to be published in the March-April issue of the *American Mineralogist*.

The ballots for officers of the Society and for candidates for fellowship will be sent out from the Secretary's office early in October.

C. S. HURLBUT, JR., *Secretary*.

To the Editor:

On page 235, vol. 29 of your journal, you published a paper by V. L. Bosazza on "Notes and news on the adsorption of some organic dyes by clays and clay minerals."

In this paper the author states that the results of Hauser and Leggett (*Jour. Am. Chem. Soc.*, **62**, 1811 (1940)) cannot be widely accepted because the clays used in their investigations are not specified in any way.

The Wyoming bentonite we used was of the highest possible purity, containing particles not over .1 micron obtained by supercentrifugal fractionation. For the reactions carried out with dry bentonite, the same purified clay was used which had been dehydrated at a temperature just below the point where x-ray analysis reveals a decomposition of the original crystal lattice. Our samples were, therefore, at least as well defined as those Mr. Bosazza used and certainly purer. That some of the color reactions we reported do not depend on the presence of water was illustrated by our use of dimethylaniline. This chemical was not used by Mr. Bosazza so that his conclusion (2) is unjustified.

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THE MINERALOGICAL SOCIETY
LONDON

6/9/44

Dear Mr. President,

May I express to you and ask you to convey to your colleagues on the Council of the Mineralogical Society of America and to its Fellows and Members the sincere sympathy of my colleagues and myself at the loss you have sustained through the tragic death of your Vice-President, Harry Berman, of whose death in the aeroplane crash at Prestwick I was informed today by our Editor, Dr. Sepnecr.

I have heard no details, but I feel certain that Dr. Berman must have been travelling to this country, if not on Government business, on business intimately connected with the war effort, and if that was the case, he is, I think, the first Officer or Member of Council of either of our twin Societies to lose his life in our countries' common cause.

I have never had the pleasure of meeting Dr. Berman, who was also a member of this Society, but his name is well known to me. Unfortunately I have never been able to visit the United States, though I have just set foot in it when travelling through from Montreal to St. John, New Brunswick, if I remember correctly at a place called Moose Lake.

With deepest sympathy

Yours sincerely,
(Signed F. N. Ashcroft)
President.

Prof. R. C. Emmons
President, Mineralogical Society of America
University of Wisconsin
Madison, Wisconsin, U.S.A.

Dr. Harry Berman, associate professor of mineralogy and curator of the Mineralogical Museum at Harvard University was killed in an airplane accident at Prestwick, Scotland, on August 27. He was on leave of absence from the University and was in charge of research laboratories and of crystal production for the Reeves Sound Laboratories, Inc., and the Hudson American Corporation. He was en route to England to supervise special war work when the crash occurred. Dr. Berman was forty-two years of age and in December

was elected Vice-president of the Mineralogical Society for the current year. A memorial will appear in a later issue of the Journal enumerating some of his important contributions to mineralogy and crystallography.

As this issue goes to press word has been received of the sudden death of Professor J. Ellis Thomson, Head of the Department of Mineralogy in the University of Toronto, on Sept. 26, 1944, at the age of sixty-two. Professor Thomson had served on the Council of the Mineralogical Society of America, also as Vice-President of the Society in 1935, and as President in 1938. A memorial will appear in a later issue.

The State Mineralogist of California announces the publication of Bulletin No. 126—California Mineral Production for 1942. It contains 224 pages, 7 illustrations and one chart, bound in paper covers. It may be purchased from the State Division of Mines, Ferry Building, San Francisco, California, for 75¢ plus 2¢ sales tax for California residents.

Announcement is also made of the *California Journal of Mines and Geology* for July 1943 (vol. 39, no. 3). Articles in this report include Crestmore minerals, the isometrograph as developed and used at the new Idria quicksilver mine, the sillimanite group of minerals, activity in strategic minerals in the Sacramento and Redding fields, and other articles. Price 60¢, plus 2½% sales tax for California residents.

Bulletin 151 of the Arizona Bureau of Mines, Geological Series (No. 16) was issued in October 1943. This 160 page bulletin deals with the Geology and Ore Deposits of the Superior Mining Area, Arizona (located in the northeastern part of Pinal County). The authors are M. N. Short, F. W. Galbraith, E. N. Harshman, T. H. Kuhn, and Eldred W. Wilson. This bulletin is distributed free to residents of Arizona, to others the price is \$1.85. Address the University of Arizona, Tucson, Arizona.

Mr. Fred W. Cassirer addressed the Philadelphia Mineralogical Society on June 1, 1944. He spoke on "Mineral Hunting in Central Europe." Mr. John Cochrane described his recent visit to the Harding Mine near Dixon, New Mexico, now being worked for microlite

The newly elected officers of the New Jersey Mineralogical Society include:
President: Joseph D'Agostino
Vice-Presidents: H. E. Millson and Dr. H. P. Walther
Treasurer: Miss E. Heusel
Secretary: G. R. Stilwell
Librarian: A. A. Surina
Curator: Dr. A. C. Hawkins.

Correction

The legends of figures 1 and 2, page 300, of the article on "Occurrence of gabbro-wehrlite near Lochalsh, Ontario" in the July-August issue of *The American Mineralogist* should read "gabbro-wehrlite" instead of "gabbro-lherzolite."

BOOK REVIEWS

OPTICAL WORKSHOP PRINCIPLES. A translation of "LE TRAVAIL DES VERRES D'OPTIQUE DE PRÉCISION" by COL. CH. DÉVÉ, Hon. Dir. of the Institut d'Optique theorique et appliquée, Paris, transl. by THOS. L. TIPPELL; pp. 306+xiv, figs. 120, 14½×22 cm., cloth. Published by Adam Hilger Ltd., London, 1943, price \$6.00, obtainable in U.S.A. from the Jarrell-Ash Co., 165 Newbury St., Boston, Mass.

This book is the second substantial one devoted to optical workmanship sponsored by Hilger Ltd. in their liberal policy of promoting availability to the public of knowledge in this field. The first was Twyman's "Prism and Lens Making"—reviewed in the *Am. Mineralogist*, 28, 400 (1943).

The French original of this second book has long been in use as a résumé of the technical instruction given to students in the trade school for working opticians of the Institut d'Optique and to the foremen and opticians who come to improve themselves at the Institut. It is not intended as a manual for beginners.

Among the subjects treated are Lenses, Abrasives, Tools, Surfacing, Mechanical Theory of Optical Working, Optical Testing, Crystal Shaping, Centering, Engraving, Metallization of Mirrors. There is considerable duplication with regard to the aforementioned book by Twyman of the subjects which are treated in the two books, but each subject presents a wide variety of aspects and the emphasis upon these aspects differs. The translation now submitted of the treatise by Col. Dévé thus constitutes a highly welcome further addition to the literature of the field.

CHARLES F. MEYER
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University of Michigan*

SOIL AND PLANT ANALYSIS by C. S. PIPER, 15×22 cm., pp. xiv and 368, 19 figs.

This represents a monograph from the Waite Agricultural Research Institute, University of Adelaide, South Australia. The original edition appeared in 1942 but the authorized photo reprint in U.S.A. by the Interscience Publishers, Inc., New York, appeared in 1944. Price \$4.50.

This publication from "the land down under" is an excellent laboratory manual for the modern quantitative analysis (physical and chemical) of soils and of the inorganic constituents of vegetable matter.

Its two main parts are sufficiently indicated by the title. The first section of 250 pages has fourteen chapters dealing with (1) the collection and preparation of soil samples (6 p.); (2) determination of hydrogen ion concentration, conductivity and water soluble salts (39 p.); (3) mechanical analysis (32 p.); (4) single value constants, such as water holding capacity, moisture equivalent, heat of wetting, etc. (31 p.); (5) soil color (4 p.); (6) preparation of standard solutions and indicators (10 p.); (7) calcium carbonate determination (8 p.); (8) the analysis of the hydrochloric acid extract (16 p.); (9) exchangeable ions and exchange capacity (42 p.); (10) nitrogen determination (4 p.); (11) nitrates, nitrites and ammonia (10 p.); (12) organic matter (16 p.); (13) free ferric oxide (8 p.); (14) separation and analysis of the clay fraction (11 p.).

The second part of 112 pages has four chapters on the collection and preparation of plant samples (6 p.); methods for the ashing of plant materials (17 p.); determination of the more common inorganic constituents (25 p.), and the determination of the trace-elements (60 p.). Selected references are given at the end of each chapter.

The various procedures are fully described and mostly preceded by a discussion of the rationale for the determination itself, together with the necessary precautions to be taken, if any. The methods are the latest that have been worked out mostly in Australia and the British Empire, so that they represent valuable adjuncts to those described in the "Official and Tentative Methods of Analysis of the (American) Association of Official Agricultural Chemists."

Although the manual is primarily destined for agricultural chemists and pedologists, nevertheless many chapters are considered well worth the attention of sedimentary mineralogists and petrologists.

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